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MOE Toxic Chemical Emission Inventory for Ontario and Eastern North America

A Final Report to:

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Ontario Ministry of the Environment
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Rexdale, Ontario
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1. SUMMARY

Atmospheric transport and deposition is considered to be an important pathway by which many toxic, persistent aromatic and organochlorine compounds enter the Great Lakes and other water bodies. However, for several of the semi-volatile organic contaminants, only limited information exists regarding emission estimates, relative source contributions and deposition mechanisms that are needed to explain the widespread (but generally low-level) occurrence in environmental media. The overall purpose of this Ontario Ministry of the Environment study is to compile a preliminary toxic compound emission inventory with spatial and temporal resolution for Ontario and Eastern North America to be used as input primarily for short-range (long-term) air quality models and to provide data for toxic chemical management/control strategy planning in Ontario. The species of concern are: 34 selected polycyclic aromatic hydrocarbon compounds (PAH), high molecular weight congeners of polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), and approximately 30 selected organic pesticides.

In the first phase of the study, specific data and types of information available were consolidated and reviewed, and general methods for preparing spatially resolved emission inventories by sector for each pollutant category were defined. In the second phase, the inventory was compiled for the base year 1985 using various approaches identified in the first phase, published or reported emission information, information received from contacts with officials in various government agencies, and data acquired from the 1985 National Acid Precipitation Assessment Program (NAPAP) Inventory.

Point, area and open source types, most likely to represent the strongest emission sources of these contaminants, were selected based on information reviewed and, where data permitted, emphasis was directed

toward the strongest contributing sources, especially in Ontario. It is important to note that, apart from previous nationwide U.S. emission inventories for PAH and specific evaluations of PCDD/PCDF emissions, no precedent emission inventories for these contaminants were found in the information review. Speciated emission factors were consolidated and derived from published, surveyed or reported information, based primarily on source measurement data for combustion facilities. Similarly, emission algorithms were developed for meteorologically-dependent pesticide sources, based on reported analytical models, physical/chemical properties of the substances, estimated loading rates and specific climatological factors. It should be recognized that some large uncertainties are associated with the emission factors and algorithms due to emission variability, data limitations and influences of various parameters even amongst the more traditional sources.

Many of the point and area source annual base quantities (e.g. fuel consumption, production rates and/or activity level data) for Canadian (excepting Ontario) and U.S. sources, at the process (SCC) level, were used directly or derived from variable NAPAP compilations after selecting relevant sources from the computerized files. Relevant point source data (i.e. in excess of 15,000 points) have been retained. Ontario point and area source base quantity data were obtained from MOE, the area source data being on a UTM grid system. Spatially apportioned data were also available with the NAPAP files. These data, in conjunction with computer processing, were used for gridding of speciated emissions, on a sector basis outside of Ontario (127 X 127 km) modelling grid which covers Eastern North America. Similarly, temporal allocation factors, included in these databases, were processed to temporally resolve the gridded emissions by source type for seasons, days-of-the-week and by hour for use in modelling these toxic chemical emissions. For data management, manipulation and inventory computation, the toxic chemical inventory has been developed and compiled on an IBM personal computer, using the PC Focus database

management system, with separate files for each of the major inventory components (e.g. point, area and open source base quantities, emission factors and temporal factors.

On the basis of inventory results, a summarized tabulation of 'total' annual estimated emissions by pollutant class for general emission categories in Ontario and Eastern North America is shown in Table 1. It can be seen that PAH emissions predominate over the other types of combustion-related pollutants and that Ontario emissions represented approximately 3 to 11% of the total emissions in Eastern North America depending on the contaminant class. It is likely that Ontario PCDD emissions have been somewhat underestimated since data were lacking for some incineration and other potential source emissions. However, it is also possible that Eastern North America PCDD and PCDF emissions from potential sources, such as secondary copper production, have also been underestimated. The uncertainties of applying specific emission factors to certain types of point sources without thorough characterization of individual sources must be recognized. This is particularly important since a large fraction in each of these pollutant classes was found to be accounted for by relatively few types of source sectors.

The ranking of the most important sector contributions is shown in Table 2. Residential wood combustion and coal-fired electric power generating stations were determined to rank as relatively substantial emission sources of several of these toxic chemicals; wood burning accounted for a large portion of the PAH emissions. Although there is minimal primary aluminum production in Ontario, aluminum smelters were also estimated to contribute substantially to PAH emissions in other regions.

Pesticide emission estimates of constituents that are common to both Ontario and Eastern North America and that result from agricultural application and emanation from soil, are shown in Table 3 by specific

functional classes. Of these selected pesticides, estimated emissions of various herbicides were predominant, especially 2,4-D which has received widespread use and can readily volatilize depending on the formulation.

Summaries of the resulting geographical distribution of the inventory compilation, provided in three scales of detail, are shown in Figures 1 to 6.

In view of the variable grid sizes in each of these presentations (i.e., variable UTM grid in Ontario and 127 km polarstereographic grid outside), the emissions must be presented as fluxes (mass.km^{-2}.yr), in order to properly represent the spatial distribution. All fluxes are based on the 'true' grid area with map correction factors applied. In Southern Ontario, emission intensities depend on both the grid area and location; many of the point sources are located in the smallest grid sizes, which greatly enhances the flux in these grids. Except for pesticide emissions, the inventory data indicate that the greatest emission strengths generally occurred in the heavier populated areas, as might be expected, due to the anthropogenic nature of the contributing sources. However, it is important to note that the area burned by forest fires in October during 1985 was at a record low and, thus, a more significant contribution to PAH emissions would be anticipated in other years in areas of Northern Ontario.

Because of the known data limitations and unknown contributions by other potential sources, the estimated toxic chemical emissions compiled in this inventory should be regarded as preliminary totals. The inventory does, however, clearly indicate the relative importance of the various source contributions. This information, together with an assessment of relative toxicity of the inventoried compounds, provides valuable guidance for future work. Several recommendations have been made with respect to future efforts in preparing a more complete and accurate inventory so as to provide further information on the occurrence and distribution of such contaminants.

TABLE 1

**Estimated Total Pollutant Class Contributions
by General Emission Category
for Ontario and Eastern North America**

Emission Category		Estimated Annual Emissions (kg)* PAH	PCB	PCDD	PCDF
Industrial	Ontario	82,300		2.44	13.16
	ENA	2,704,000		3.01	14.6
Stationary Fuel Combustion	Ontario	155,000	12.2	2.38	6.24
	ENA	4,545,000	451	72.7	118
Solid Waste Incineration	Ontario	670	1.3	4.19	6.28
	ENA	48,500	42	105	85.6
Transportation	Ontario	24,500		0.041	0.058
	ENA	1,174,000		3.50	4.96
Open Sources	Ontario	9,150	36.9	0.007	0.009
	ENA	926,000	517	2.72	3.85
Total	Ontario	271,600	50.4	9.07	25.7
	ENA	9,397,400	1,010	187	227

* Values after rounding

TABLE 2

Important Contributing Sectors by Pollutant Class

Relative Source Strength Rank	Pollutant Class	Ontario	ENA
1	PAH	Residential Wood Comb.	Residential Wood Comb.
2		Ferroalloy Production	Primary Aluminum Prod.
3		Metallurgical Coke Prod.	Industrial Fuel Comb.
4		On-Road Diesel Vehicles	Ferroalloy Prod.
5		Light-Duty Gasoline Vehicles	Prescribed Burning
1	PCB	Transformer Leakage	Transformer Leakage
2		Electric Power Generation	Electric Power Generation
3		Industrial Fuel Comb.	Industrial Fuel Comb.
4		Landfills	Landfills
5		Sewage Sludge Incin.	Waste Oil Comb.
1	PCDD	Municipal Waste Incin.	Industrial Waste Incin.
2		Secondary Copper Prod.	Industrial Wood Comb.
3		Residential Wood Comb.	Residential Wood Comb.
4		Industrial Fuel Comb.	Municipal Waste Incin.
5		Electric Power Generation	Electric Power Generation
1	PCDF	Secondary Copper Prod.	Residential Wood Comb.
2		Municipal Waste Incin.	Industrial Waste Incin.
3		Residential Fuelwood Comb.	Electric Power Generation
4		Electric Power Generation	Municipal Waste Incin.
5		Sewage Sludge Incin.	Industrial Wood Comb.

TABLE 3

Estimated Speciated Pesticide Emissions in Ontario and Eastern North America

		Estimated Emissions (kg)* Ontario	ENA
Herbicides			
	Alachlor	195,200	7,243,000
	Atrazine	220,700	4,874,000
	Butylate	8,950	13,200**
	Cyanazine	60,000	1,534,000
	2,4-D	184,800	10,691,000
	Linuron	99,900	108,700**
	Metolachlor	156,900	3,646,000
	Metrabuzin	51,500	58,900**
	MCPA	52,400	568,200**
	Trifluralin	9,520	2,058,000
	Total	1,039,900	30,795,000
Insecticides			
	Carbaryl	19,650	1,872,000
	Carbofuran	7,410	982,700
	Chlordane	354	853**
	Diazinon	8,580	219,600
	Endosulfan	7,300	11,300**
	Lindane	2	2,570**
	Methoxychlor	1,390	2,110**
	Total	44,680	3,091,000
Fungicides			
	Captan	78,030	132,300**
Nematocides			
	Chloropicrin	58,400	59,800**
	Dichloropropenes/propanes	1,296,300	1,330,100**
	Methylisothiocyanate	185,800	185,800**
	Total	1,540,500	1,575,700

* Values after rounding
** Data not available in the U.S.

Figure 1

Annual Area Source Emissions of PAH in Southern Ontario

Figure 2

Annual Emissions of Insecticides in Southern Ontario

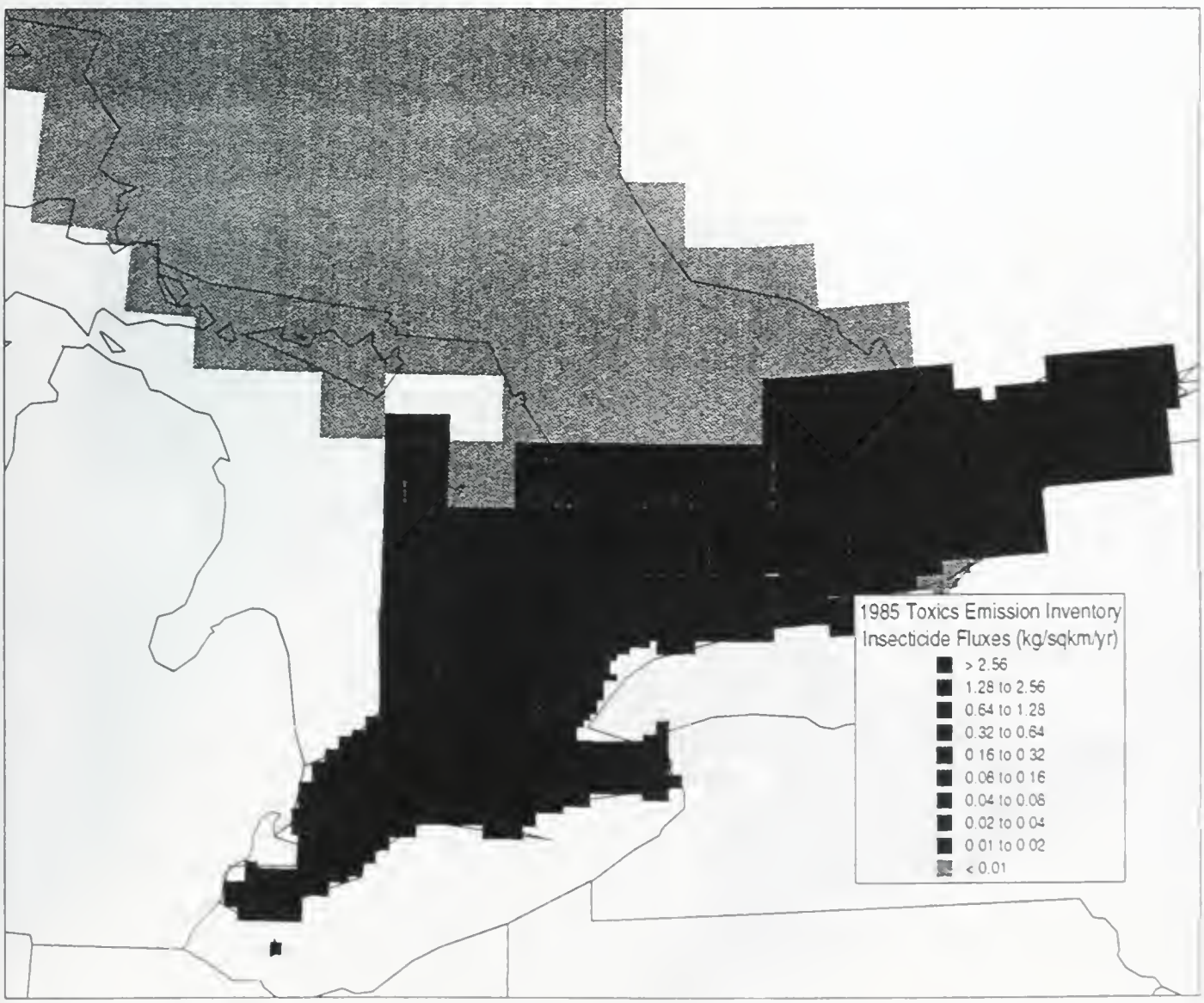


Figure 3

Annual Area Source Emissions of PAH in Ontario

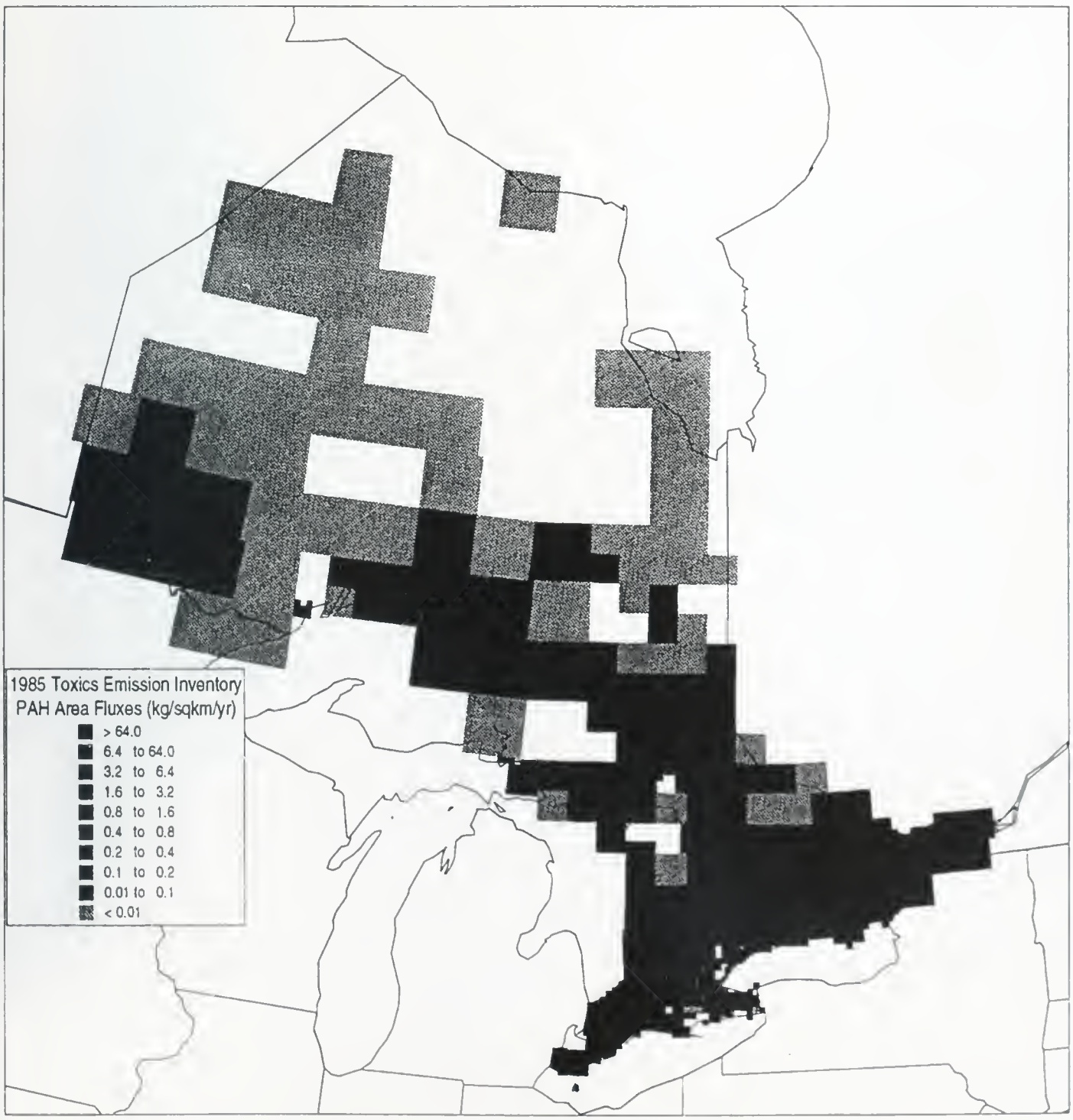


Figure 4

Annual Area Source Emissions of PCDD in Ontario

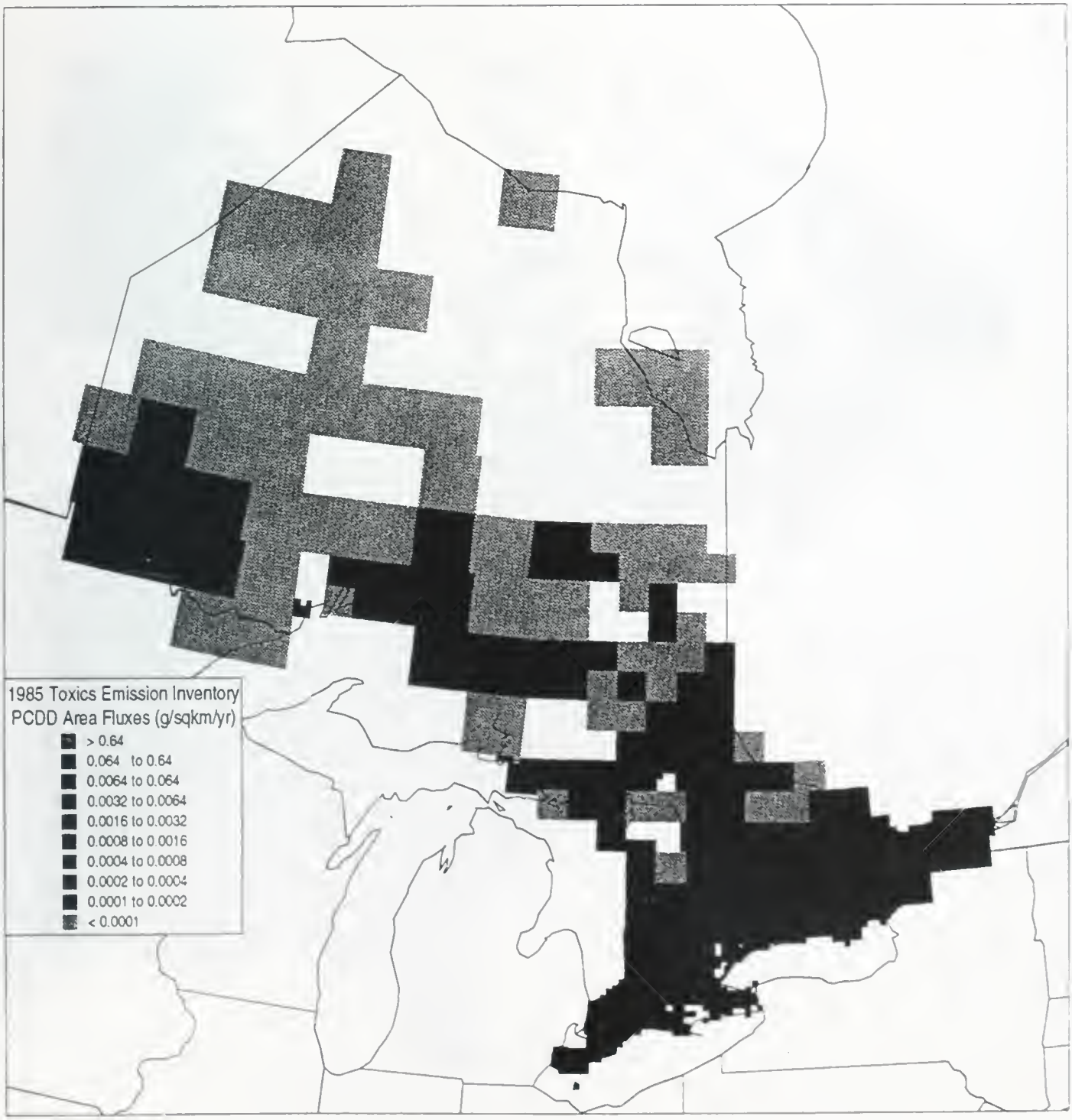


Figure 5

Annual Area Source Emissions of PAH in Eastern North America

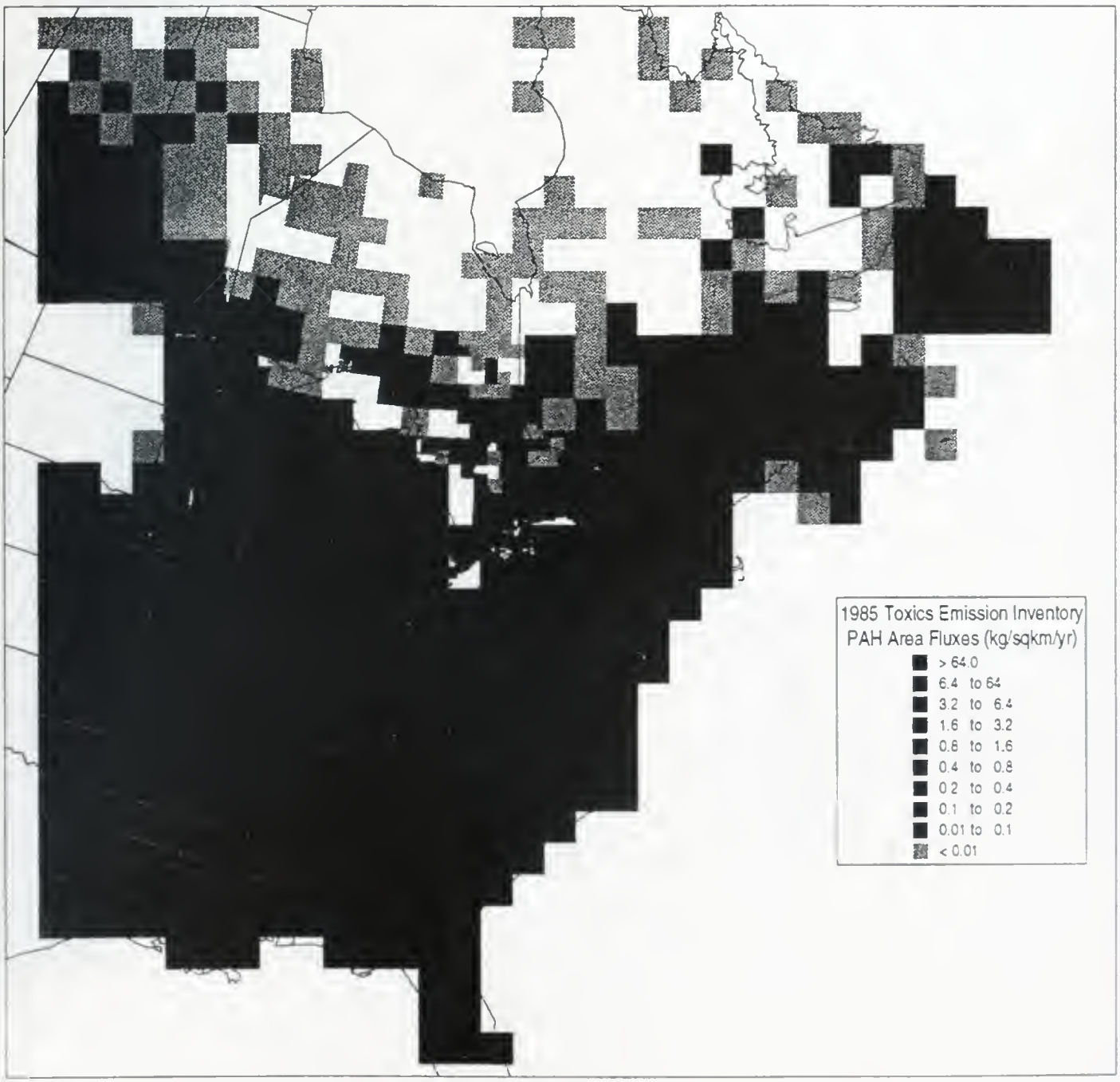
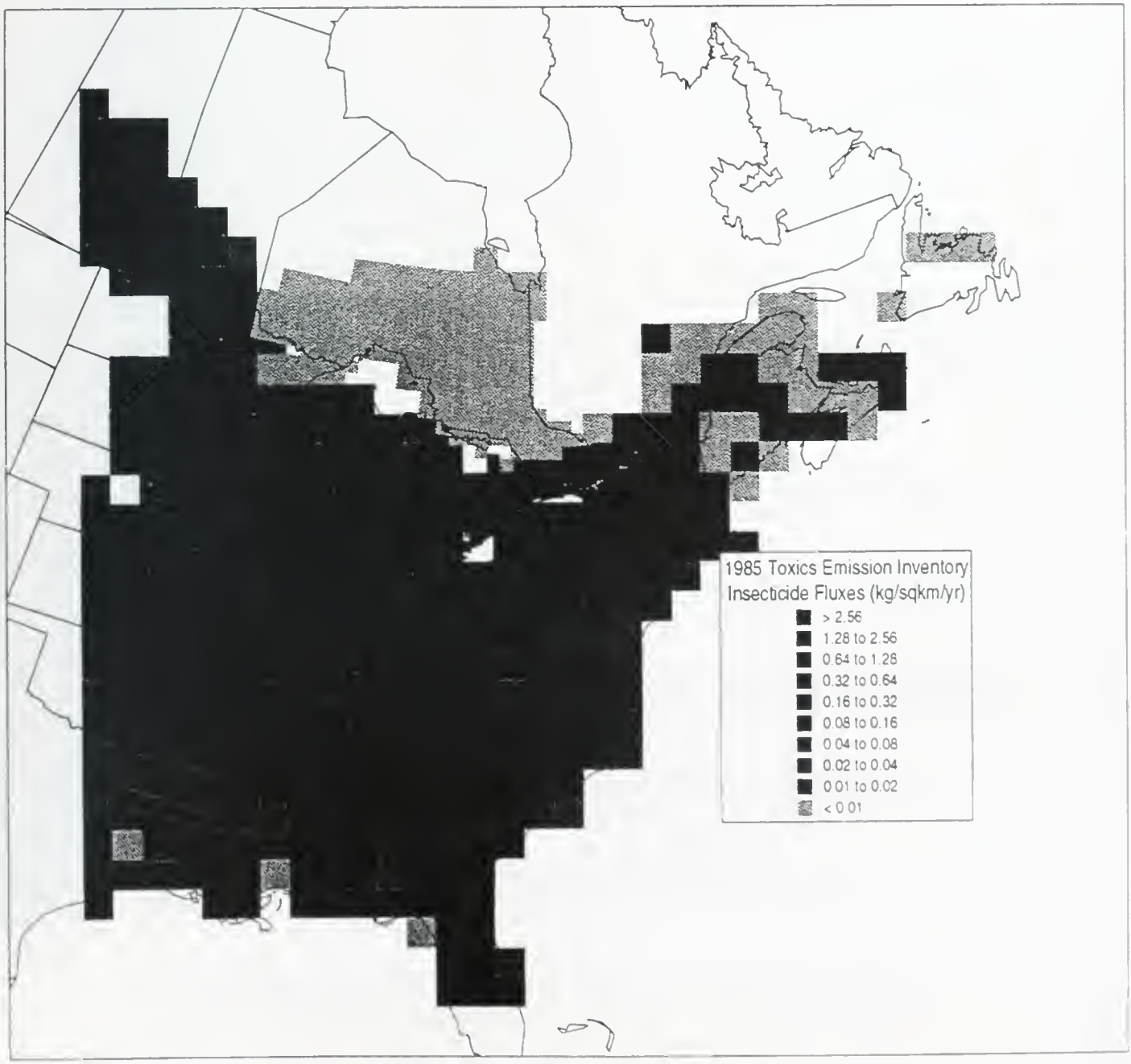


Figure 6

Annual Emissions of Insecticides in Eastern North America



2. INTRODUCTION

2.1 Study Needs and Purpose of the Inventory

In recognition of the potential health effects and increasing environmental concern regarding the occurrence of toxic chemicals in various environmental media, the Ontario Ministry of the Environment has prepared a preliminary but comprehensive toxic chemical emission inventory to define the source types, locations and emission rates for a variety of toxic chemicals in Ontario and Eastern North America. The high risk pollutant groups which have been identified for this inventory and future overall assessment of environmental impact include: various pesticides, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polynuclear aromatic hydrocarbons (PAHs). The major purposes for developing an Ontario and Eastern North American inventory and uses are:

- to identify and quantify toxic compound emissions from potential sources within and outside of Ontario on a first cut basis as input for short-range (long-term) air quality model assessments,
- to provide means to determine relative source strengths and define regions of greatest estimated emissions,
- to provide a basis for future investigation studies where important data gaps exist or where estimation methods are inadequate relative to the importance of the source,
- to identify trends in usage, storage and discharge of toxic compounds in Ontario and other regions that may affect air quality in Ontario,
- to provide data and assessments that will assist in the management of toxic chemicals and control strategy planning.

It is recognized that most of the toxic chemical compounds of concern in this study are introduced into the environment by anthropogenic activities, since

most of these do not result from natural sources nor occur naturally. Exceptions to this are toxic components that are emitted in open wildfires (e.g. PAH constituents). In addition, primary emissions of anthropogenic origin can occur from natural media such as open water and soil. Many of these compounds are stable and can persist for long periods of time in the parent toxic form and some can be formed during combustion. Despite a general growth of environmental concentration information, many uncertainties exist regarding potential adverse health effects associated with long-term, low-level exposure, the degree to which such compounds constitute an air pollution hazard, and the primary routes of entry to humans. Nevertheless, atmospheric deposition is surmised to be the predominant input pathway of most of these compounds to land and water surfaces. Accordingly, there is a need to determine the relative contribution of atmospheric input to pathways of human exposure and the general contamination of environmental media. Hence, the need for compiling accurate emission inventories is evident since inventory data can be used in setting program priorities and such information provides a primary tool in the overall assessment of toxic chemical management. Because strong geographical variations in emissions can exist, the knowledge of source locations with emission strengths is required for purposes of modelling and control strategy development.

2.2 Program Objectives

The major objective of this study was to prepare a comprehensive but first cut emission inventory for a variety of selected toxic chemicals by defining the source types, emission rates and spatial distribution of emissions in Eastern North America with greater emphasis on Ontario emissions. The contaminants selected for this inventory were primarily semi-volatile organic compound classes since inventories of volatile organic compounds have already been prepared.

The specific project objectives were:

- to conduct a thorough literature and database review with procurement, extraction and consolidation of relevant emission-related information from available sources,
- to compile an emission inventory of selected toxic chemical classes (with speciation) for the base year 1985 and resolve emissions to the variable MOE grid system in Ontario as well as 127 x 127 km grids in other provinces and states in Eastern North America. The inventory is to include point, area and open sources for all sectors and processes which are major toxic chemical contributors,
- to generate or consolidate pertinent seasonal, weekly and diurnal (24-hour) temporal factors by source/sector type applicable to the toxic chemical release,
- to indicate data uncertainties on the emission estimates compiled by sector,
- to generate a computerized emission inventory database that can be accessed and updated using PC Focus database system,
- to make provisions to transfer the variable UTM grid inventory in Ontario to a 127 x 127 km grid to provide a gridded Eastern North America modelling inventory.

3. OVERVIEW OF INVENTORY REQUIREMENTS AND TECHNIQUES

3.1 General Overview and Scope

The overall intent of the inventory was to quantify selected toxic compound emissions from sources within and outside of Ontario using available published information. After conducting Phase I of the study, to identify sources of information and general approaches (ORF/MEP 1987), the inventory has been compiled in Phase II. The base year of 1985 was selected for development of the toxics inventory since this base year was used for generating other North American emission inventories which are reported to be the most accurate compilations to date. Information was consolidated and reviewed for all potentially contributing source sectors at the process level. The area of coverage includes all provinces east of the Alberta/Saskatchewan border, and all states east of (and bordering on) the Mississippi River and south to Florida in accordance with the established air pollutant modelling area for Eastern North America.

As the study scope was particularly wide and the inventory could be developed at practically any level of detail, an appropriate degree of priority for the various tasks was established in order to accomplish the program objectives. Greater emphasis was directed toward defining approaches and compiling/apportioning emissions for the major sources in Ontario than for other provinces and states. Similarly, emphasis was placed on sources that were generally regarded to be the strongest emission sources. However, in some instances, it was difficult in advance to identify or rank the strongest sources based on existing information (e.g. PCB emissions). Because this represents a first attempt at compiling an inventory for many of these semi-volatile pollutants and it was known that emission factors for several of the pollutants and suspected source types were not readily available, the inventory must be regarded as a first-cut, preliminary database.

An overview of the strategy for conducting the inventory is shown in Figure 3.1. This shows the general components or tasks involved in determining the emission estimates and processing the inventory information with each discussed in sections that follow. Base quantity information for many of the Canadian (excluding Ontario) and U.S. sources inventoried was available from the conduct of the 1985 National Acid Precipitation Assessment Program (NAPAP) inventory and this comprehensive database was used extensively in view of its reported accuracy. Base quantity data for Ontario were supplied by the Ontario Ministry of the Environment.

The types of emission categories, sectors and contributing processes included in the inventory are summarized in Table 3.1.1. The assignment by point, area or open source for each process is noted along with the primary data sources used to generate base quantity or process activity data. Similarly, the types of pollutants compiled for each process are summarized in this tabulation. In addition, a list of Master Sector Codes (MSC) developed for this study and corresponding Source Classification Codes (SCC) that have been developed in other inventories are tabulated in the appendix. These have been combined for reporting total emissions by sector but all emissions have been estimated and processed at the SCC level for the inventory. It should be noted that a different SCC coding system is used for Ontario, Canadian and U.S. area sources but is common for most point sources.

Figure 3.1

General Inventory Development Approach

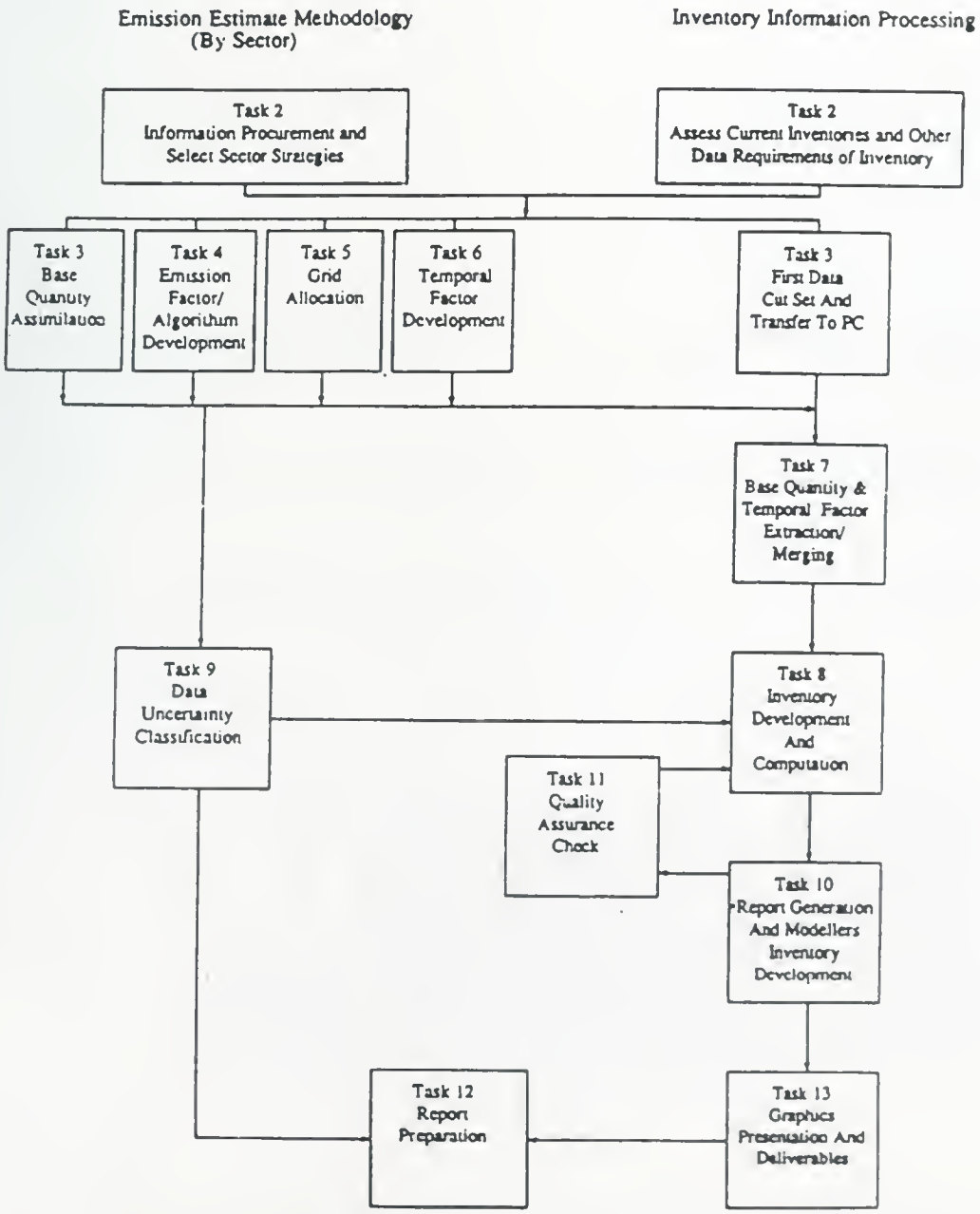


TABLE 3.1.1
Inventory Summary[1]

Master Sector Number	Sector Description	Base Quantity[2,3] Ont.	Can.[4]	U.S.	Pollutant Emissions PAH	PCDD	PCDF	PCB	Pest.
INDUSTRIAL									
10101	Metallurgical Coke Production	OP	NP	NP	•				
10201	Iron and Steel Production	OP	NP	NP	•				
10301	Ferrous Foundries-Cupola and other	OP	NP	NP	•				
10302	Ferrous Foundries-Induction/EAF's and Other	OP	NP	NP	•				
10401	Ferroalloy Production-Open Furnace	OP	NP	NP	•				
10402	Ferroalloy Production-Semi-covered Furnace	OP	NP	•					
10501	Aluminum Production-Pre-Bake Anode Process	OP	NP	•					
10502	Aluminum Production-Horizontal Soderberg	OP	NP	•					
10503	Aluminum Production-Vertical Soderberg	OP	NP	•					
10701	Carbon Black Manufacture-Gas Furnace	-	NP	•					
10702	Carbon Black Manufacture-Oil Furnace	OP	-	NP	•				
10801	Wood Charcoal Production	-	NP	•					
10901	Petroleum Refining	OP	NP	NP	•				
11001	Asphalt Roof.Man-Blowing	OP	NP	•					
11002	Asphalt Roof Man./Storage	-	NP	•					
11101	Asphalt Hot Mix	OA,P	NA	NP	•				
11201	Kraft Pulping-Black Liquor	OP	NP	NP		•	•		
11301	Secondary Copper Prod.-Cupola	OP	NP	•	•				

TABLE 3.1.1 (Cont'd)
Inventory Summary[1]

Master Sector Number	Sector Description	Base Quantity[2,3]			Pollutant Emissions				
		Ont.	Can.[4]	U.S.	PAH	PCDD	PCDF	PCB	Pest.
STATIONARY FUEL COMBUSTION									
20101	Elec. Power Gen.-Anthracite	-	-	NP	•	•	•		
20101	Elec. Power Gen.-Bit., Sub.	OP	NP	NP	•	•	•	•	
20103	Elec. Power Gen.-Lignite	OP	NP	NP	•	•	•		
20104	Elec. Power Gen.-Residual Oil	-	NA,NP	NP	•	•	•		
20105	Elec.Power Gen.-Distillate Oil	OP	NA,NP	NP	•	•	•		
20106	Elec.Power Gen.-Natural Gas	OP	NP	NP	•	•	•		
20201	Ind. Fuel Comb.-Anthracite	-	-	NA,NP	•	•	•	•	
20202	Ind. Fuel Comb.-Bit.,Sub.	OA,OP	NA	NA,NP	•	•	•	•	
20203	Ind. Fuel Comb.-Lignite	-	-	NP	•				
20204	Ind. Fuel Comb.-Residual Oil	OA,OP	NA,NP	NA,NP	•				
20205	Ind. Fuel Comb.-Distillate Oil	OA,OP	NA	NA,NP	•				
20206	Ind. Fuel Comb.-Natural Gas	OA,OP	NA,NP	NA,NP	•				
20301	Comm./Inst.Fuel Comb.-Anthracite	-	-	NA,NP	•				
20302	Comm./Inst.Fuel Comb.-Bit., Sub.	-OP	NA	NA,NP	•				
20303	Comm./Inst.Fuel Comb.-Lignite	-	-	NA,NP	•				
20304	Comm./Inst.Fuel Comb.-Residual Oil	OA,OP	NA	NA,NP	•				
20305	Comm./Inst.Fuel Comb.-Distillate Oil	OA,OP	NA	NA,NP	•				
20306	Comm./Inst.Fuel Comb.-Natural Gas	OA,OP	NA	Na,NP	•				
20401	Res. Fuel Comb.-Coal	-	NA	NA	•	•	•		
20402	Res. Fuel Comb.-Residual Oil	OA	NA	NA	•	•	•		
20403	Res. Fuel Comb.-Distillate Oil	OA	NA	NA	•	•	•		
20404	Res. Fuel Comb.-Natural Gas	OA	NA	NA	•				
20501	Res. Wood Comb.-Stove	OA	NA	NA	•	•	•		
20502	Res. Wood Comb.-Fireplace	OA	NA	NA	•	•	•		
20503	Res. Wood Comb.-Wood Furnace	-	NA	-	•	•	•		

TABLE 3.1.1(Cont'd)
Inventory Summary[1]

Master Sector Number	Sector Description	Base Quantity[2,3] Ont.	Can.[4]	U.S.	Pollutant Emissions PAH	PCDD	PCDF	PCB	Pest.
20601	Other Wood Comb.-El. Pwr. Gen.	-	-	NP	•	•	•		
20602	Other Wood Comb.-Industrial	OA,OP	-	NA,NP	•	•	•		
20603	Other Wood Comb.-Comm./Inst.	-	-	NP					
20701	Internal Comb.-Dies.Turbines	-	NP	NP	•				
20702	Internal Comb.-Dies. Recip.	-	NP,NA	NP	•				
20703	Internal Comb.-Dies.Lrg.Bore Eng.	-	-	NP	•				
20704	Internal Comb.-Gasoline	-	-	NP	•				
WASTE INCINERATION									
30101	Municipal Waste Incineration	OA,OP	NP	NP	•	•	•	•	
30201	Sewage Sludge Incineration	OA,OP	-	NP	•	•	•	•	
30301	Ind. Waste Inc.-Mix Liq.	OP	-	NP	•	•	•	•	
30302	Ind. Waste Inc.-Mix Sol.	NA,OP	NA	NP	•	•	•		
30303	Ind. Waste Inc.-Wood Comb.	OA,OP	NA	NP	•				
30304	Ind. Waste Inc.-Wire Inc.	-	-	NP		•	•		
30401	Comm./Inst.Waste Inc.-Mix Liq.	-	-	NP	•	•	•	•	
30402	Comm./Inst.Waste Inc.-Mix Sol.	OA,OP	-	NP	•	•	•	•	
30403	Comm./Inst.Waste Inc.-Pathological	OP	-	NP	•	•	•	•	
30501	Waste Oil Comb.-El. Pwr.Gen.	-	-	NP	•			•	
30502	Waste Oil Comb.-Industrial	-	-	NP	•			•	
30503	Waste Oil Comb.-Comm./Inst.	-	-	NP	•			•	
TRANSPORTATION									
40101	Light Duty Gasoline Vehicles	OA	NA	NA	•	•5	•5		
40201	Heavy Duty Gasoline Vehicles	OA	NA	NA	•	•	•		
40301	Off-Road Gasoline Vehicles	OA	NA	NA	•	•	•		
40401	Heavy Duty Diesel Vehicles	OA	NA	NA	•				
40501	Off-Road Diesel Vehicles	OA	NA	NA	•				

TABLE 3.1.1(Cont'd)
Inventory Summary[1]

Master Sector Number	Sector Description	Base Quantity[2,3]			Pollutant Emissions				
		Ont.	Can.[4]	U.S.	PAH	PCDD	PCDF	PCB	Pest.
40601	Aircraft-LTO's	OA	NA	NA	•				
40701	Railroad	OA	NA	NA	•				
40801	Vessels-Coal	-	-	NA	•				
40802	Vessels-Diesel Oil	OA	NA	NA	•				
40803	Vessels-Residual Oil	OA	NA	NA	•				
40804	Vessels-Gasoline	-	-	NA	•	•	•		
OPEN SOURCES									
50101	Open Burning-Residential	-	-	NP,NA	•				
50102	Open Burning-Industrial	-	-	NP,NA	•				
50103	Open Burning-Comm./Inst.	-	-	NA	•				
50201	On-Site Incin.-Residential	-	-	NA	•				
50202	On-Site Incin.-Industrial	-	-	NA	•	•	•		
50203	On-Site Incin.-Comm./Inst.	-	-	NA	•	•	•	•	
50301	Forest Fires	OA	NA	NA	•	•	•		
50401	Prescribed Burning	OA	NA	NA	•	•	•		
50501	Pesticide Use	S	S	S					•
50601	Transformers	S	S	S				•	
50701	Municipal Refuse-Landfill	S	S	S		•			

Notes

1. A=area, P=point, N=NAPAP, O=MOE, S=special.
2. Area source base quantity data from NAPAP and the MOE inventories were already gridded. NAPAP data for the U.S. was available on a county level. NAPAP data for Canada was on a provincial basis. These were gridded using surrogate data provided by Env. Canada . MOE area source data were available on the MOE UTM grid.
3. Temporal factors were not available for Canadian area source data. Michigan temporal factors were assigned to NAPAP data for Canada and MOE data for Ontario as appropriate .
4. Refers to Canada less Ontario.
5. Leaded gasoline only.

3.2 Selection of Chemical Components

The selected chemical compounds included in the inventory with corresponding Chemical Abstract Service Registry System (CAS) identification codes are shown in Table 3.2.1. For PCBs, dioxins and furans, the CAS codes represent congener groups rather than specific isomers and for pesticides, the codes are for the active ingredient only. Most of these chemicals are semi-volatile, persistent compounds of mid to high molecular weight that may be emitted in the particulate or vapour phase (or may readily adsorb on airborne particulate matter). Most are considered to be toxic to various life forms, many are reputed to be carcinogenic in varying degrees and many are known to bioaccumulate/biomagnify. The usage of some of these materials (e.g., certain pesticides, PCBs) has been restricted or banned by various North American regulations. However, there are still potential pathways by which these can enter the atmosphere and/or recycle between environmental compartments. Only primary emission mechanisms, however, have been included in the inventory (see Section 8). In addition, there is evidence to indicate that some of these toxic chemicals (e.g., PAH, PCDD, PCDF) form during combustion processes. Hence, it can be expected that emissions depend at least partly on combustion operating conditions (which may vary widely between sources) rather than the presence of the toxic in the fuel/feed/input to the combustion process.

Because of the numerous types of pesticides in use, some selection of chemical constituents of primary importance has been done in order to prepare and maintain a manageable inventory. For example, the list of pesticides shown (comprising insecticides, herbicides, fungicides and nematocides) has been selected from approximately 135 types reported to be applied to various types of vegetation in Ontario during 1983 (McGee 1983). This preliminary group was selected on the basis of criteria such as: the largest amounts applied in Ontario, toxicity data (Lee 1976), those that may possibly exist in air (Lee 1976), those currently monitored in the Ontario

acid precipitation network, those found to be most prevalent in ambient air near US households (Lewis 1986), and those found in the Great Lakes with known or uncertain toxicity (Great Lakes Science Advisory Board 1981). In addition, a ranking scheme developed by Midwest Research Institute in 1978 (Kelso et al 1978) for several of these pesticides was applied to facilitate/confirm selection based on the following criteria that were given equal weighting:

- extent of application in Ontario
- mammalian toxicity
- wildlife toxicity
- special toxicity
- bioaccumulation and mobility
- environmental persistence

On the basis of the total scoring, it was apparent that some pesticides on this list were of marginal significance such as metolachlor and cyanazine. However, these were retained due to the rather extensive use in Ontario.

Total PCBs includes trichlorinated biphenyls and all higher molecular weight congeners. Dioxin and furan emissions include tetra- to octa-chlorinated dibenzo-p-dioxins and dibenzofurans. Generally, it has not been possible to inventory separate congeners of PCBs but, where data were available, separate congeners are reported. A list of 34 polycyclic aromatic hydrocarbon compounds were identified to be inventoried including selected nitro-PAH compounds. Naphthalene is not included. Aggregated emissions of benzo(a)pyrene have been estimated for several sources in both Ontario (MOE 1979) and Canada (NRCC 1983) and generally most information (e.g., measurements) is available for this compound. However, there are several recognized limitations of using B(a)P as an indicator of total PAH with which to update emissions data: it may only be a small fraction of total PAH emissions, it may not necessarily correlate with other compounds present in emissions and it is reactive. In this regard, more

recent attention has been directed toward identifying and characterizing a number of PAH species in source emissions (Bergstrom et al 1981, Larsen 1984). Similarly, because there is no standard definition of the constituents that comprise "total PAHs" and investigators often report total PAH without listing compound types: this has been noted where such data are used. In all instances, preference has been given to using measurement data in which both gas and particle phases have been determined or otherwise noted.

Although chemically speciated emissions have been estimated where possible for this inventory, there are currently insufficient data to quantify emissions according to particle size or physical form. It is recognized that characteristics such as these are required for modelling the behaviour and fate of these contaminants in the atmosphere. However, physical changes to many of these semi-volatile species might be expected to occur either during or soon after initial release from a primary source. For example, at least portions of the vapours that exist during high temperature combustion operations or other volatilization processes are anticipated to readily condense or adsorb on particulate matter after initial release. It follows that in-stack source measurements (using filters/adsorbers to collect particulate/ vapour fractions) may accurately indicate the total emissions of such species but (depending on the measurement location, temperature, etc.) may not accurately represent vapour/particle or particle size distribution of compounds that are actually emitted or exist a short distance from the source. Perhaps near-source ambient measurements or other compound-specific theoretical estimates would be more useful to derive physical distributions or particle-associated fractions of such compounds than source test data. On the other hand, the amount, particle size and chemical characteristics of primary particulate emissions (or the type and nature of ambient particulate matter contacted by vapour after release) such as soot, ash, etc., which may affect the degree of vapour adsorption are expected to

be at least partially important factors with respect to the physical form in which these contaminants enter or exist in the atmosphere.

TABLE 3.2.1

Chemical Compounds

Group	CAS Code	Chemical
Herbicides		
	15972-60-8	Alachlor
	1912-24-9	Atrazine
	2008-41-5	Butylate
	21725-46-2	Cyanazine
	94-75-7	2,4-D
	330-55-2	Linuron
	51218-45-2	Metolachlor
	94-74-6	MCPA
	21087-64-9	Trifluralin
Insecticides		
	309-0-2	Aldrin
	63-25-2	Carbaryl
	1563-66-2	Carbofuran
	57-74-9	Chlordane
	333-41-5	Diazinon
	50-29-3	DDT's
	60-57-1	Dieldrin
	115-29-7	Endosulfan
	72-20-8	Endrin
	58-89-9	Lindane
	72-43-5	Methoxychlor
	2385-85-5	Mirex
	8001-35-2	Toxaphene
Fungacides		
	133-6-2	Captan
	8018-1-7	Mancozeb
	9006-42-2	Metiram
Nematocides		
	76-6-2	Chloropicrin
	78-87-5	Dichloropropanes
	542-75-6	Dichloropropenes
	556-61-6	Methylisothiocyanate

TABLE 3.2.1 (Contd.)

Chemical Compounds

Group	CAS Code	Chemical
Polychlorinated Biphenyls (PCB's)		
	25323-68-6	T_3CB
	26914-33-0	T_4CB
	25429-29-2	P_5CB
	26601-64-9	H_6CB
	28655-71-2	H_7CB
	55722-26-4	O_8CB
	53742-7-7	N_9CB
	2051-24-3	DCB
	1336-36-3	Tot. PCB
Polychlorinated Dibenzo-p-Dioxins (PCDD's)		
	1746-1-6	2,3,7,8-T_4CDD
	41903-57-5	T_4CDD
	36088-22-9	P_5CDD
	34465-46-8	H_6CDD
	37871-0-4	H_7CDD
	3268-87-9	OCDD
	262-12-4	Tot. PCDD
Polychlorinated Dibenzofurans (PCDF's)		
	51207-31-0	2,3,7,8-T_4CDF
	55722-27-5	T_4CDF
	30402-15-4	P_5CDF
	55684-94-1	H_6CDF
	38998-75-3	H_7CDF
	39001-2-0	OCDF
	132-64-9	Tot. PCDF
Polycyclic Aromatic Hydrocarbons (PAH's)		
	83-32-9	Acenaphthene
	208-96-8	Acenaphthylene
	120-12-7	Anthracene
	56-55-3	Benz(a)anthracene
	56832-73-6	Benzofluoranthenes
	205-99-2	Benzo(b)fluoranthene

TABLE 3.2.1 (Contd.)

Chemical Compounds

Group	CAS Code	Chemical
PAH's (Cont'd)	205-82-3	Benzo(j)fluoranthene
	207-8-9	Benzo(k)fluoranthene
	30777-18-5	Benzo(a)fluorene
	191-24-2	Benzo(ghi)perylene
	50-32-8	Benzo(a)pyrene
	192-97-2	Benzo(e)pyrene
	86-74-8	Carbazole
	218-1-9	Chrysene
	191-7-1	Coronene
	27208-37-3	Cyclopenta(cd)pyrene
	226-36-8	Dibenz(ah)acridine
	224-42-0	Dibenz(aj)acridine
	53-70-3	Dibenz(ah)anthracene
	194-59-2	7H-Dibenzo(cd)carbazole
	191-26-4	Dibenzo(def,mno)chrysene
	132-65-0	Dibenzothiophene
	42397-64-8	1,6-dinitropyrene
	42397-65-9	1,8-dinitropyrene
	206-44-0	Fluoranthene
	86-73-7	Fluorene
	193-39-5	Indeno(1,2,3-cd)pyrene
	26914-18-1	Methylanthracenes
	31711-53-2	Methylphenanthrenes
	77468-36-1	Nitrofluoranthenes
	5522-43-0	1-nitropyrene
	198-55-0	Perylene
	85-1-8	Phenanthrene
	129-0-0	Pyrene
	217-59-4	Triphenylene
	8007-45-2	Total PAH

3.3 Point, Area and Open Source Distinctions

A distinction has been made between point and area sources for each sector (see Table 3.1.1) on the basis of available inventory data for criteria pollutant emissions. For instance, point sources are generally defined as those sources large enough (i.e. with significant emissions) to permit and/or maintain individual records. Area sources are defined as small sources that are too numerous to permit or warrant individual record-keeping and are accounted for collectively. Open sources (of both anthropogenic and natural origin) are mainly those with emissions that are at least partially controlled by meteorological or climatological parameters. For some inventories, point sources may be selected on the basis of a pre-defined emission cut-off level that may relate to the toxicity of the substance. In other localized (e.g. city or regional) inventories practically all emission sources may be classified as point sources regardless of emission strength (Lahre 1986). Because the toxic component emission rates for several of the source types considered in this study have not been determined relative to each other, there was no precedent on which to base a cut-off point for designating sources to either point or area. Similarly, there was no basis with which to identify sectors that have normally been treated as area sources in other inventories that might eventually qualify as a point source in the toxic inventory. After initial consideration of source distinctions for each sector, it was decided to retain the classification for those that were traditionally treated as point sources and the NAPAP inventory was used as the basis for these assignments. This resulted in a large number of point sources being inventoried due to the large geographical coverage. As such, it is generally conceived that more extensive/detailed point source data will result in a more accurate data base.

For some pollutants (pesticides for example), it was anticipated that the emission contribution by open sources would significantly dominate industrial/combustion/transportation contributions. For this reason, considerable effort was directed toward a careful evaluation of major open

source sectors. However, from a human exposure and risk viewpoint, all potentially significant sources were considered.

3.4 Information Review and Data Acquisition Approach

In compiling emissions, most information was obtained from published reports, journal articles and discussions with personnel in various government agencies. Both computerized and manual literature searches were conducted along with a review of Air Pollution Abstracts. Similarly, recent issues of key journals were periodically reviewed in an effort to maintain an update of information as the study proceeded. Efforts were also made to acquire unpublished, draft reports where these could be released. Extensive use was made of the following reports, databases and other information:

- the 1985 NAPAP emission inventory (Version 2) primarily for base quantity information on most Canadian and U.S. sources including spatial and temporal allocation (U.S. EPA 1989b),
- MOE and Environment Canada base quantity and spatial allocation databases,
- Statistics Canada reports,
- a recent Environment Canada/MOE report in which toxic chemical emission factors were consolidated from Canadian source test information and various other reports (Johnson 1988),
- various MOE, Environment Canada and NRCC reports on emission estimates of pertinent air toxics (MOE 1985, Sheffield 1985, NRCC 1983),
- conference proceedings including APCA, EPA and other specialty meetings along with recent journal articles (i.e., emphasis on 1984-early 1989),
- the National Air Toxics Information Clearing House (NATICH) database which was searched for relevant emissions test data by sector and chemical compound (i.e., however, most data pertained to toxic VOCs and trace metals),

- several U.S. EPA reports pertinent to previous emission estimates for some components, emission factor documentation and sector assessments (Kelly, 1983, U.S. EPA 1987a, d, e, f and g, U.S. EPA 1989),
- pesticide usage data contained in specific Canadian and U.S. reports and databases (e.g. Gianessi and Puffer 1988, McGee 1984).

Contacts were made with several officials at MOE, Environment Canada and U.S. EPA to request or determine the availability of relevant information needed for the study. Although an extensive amount of information was acquired from a number of officials, efforts to obtain data from the recently-initiated National Toxic Chemical Release Inventory (TRI) database in the U.S. were not successful. Similarly, particular efforts were made to procure pesticide usage information but, due to confidentiality requirements in both Canada and the U.S., only limited direct information on consumption was available. MOE Industrial Permit Files and industrial questionnaire data were reviewed for pertinent Ontario source information. It should be noted that because information is rapidly expanding for the toxic chemicals considered in this study, it is probable that additional relevant published information has become available since literature reviews were conducted. On the basis of information found, previous North American emission estimates for the air toxics examined here were reported in the following studies:

- PAH and B(a)P emission estimates for several U.S. sources conducted in the late 1970's and early 1980's (reported in NRCC 1983, Kelly 1983, U.S. EPA 1984),
- B(a)P emission estimates in Ontario and Canada (reported in NRCC 1983),
- recent PAH and B(a)P emissions for Quebec (Environment Canada 1988),
- PCDD emissions estimated for some sources in Ontario and Canada (MOE 1984, Sheffield, 1985).

3.5 Base Quantity Compilation and Assimilation

All base quantity data for Ontario (point and area) were supplied by the MOE. As the base year 1985 was selected for the inventory, accurate base quantity information by SCC was available in the 1985 NAPAP database prepared by Alliance Technologies Corp. (U.S. EPA 1989b), for many of the pertinent Canadian (less Ontario) and U.S. point sources (see Table 3.1.1). These base quantities, stack parameters (when available) and other point source information were used directly after eliminating sources from the file that were not applicable to the pollutants of interest. However, direct base quantity or activity level data were not produced for the area sources on the NAPAP grid system and only gridded emissions of various criteria pollutants (e.g., particulate, SO_2, NOx and VOC) were available by area source SCC. These gridded emissions were generated and processed in the NAPAP inventory by apportioning calculated annual emissions from fuel use or operating rate data at the national or state level to counties using appropriate surrogate spatial distribution factors (e.g., population, housing, employment statistics, satellite land use data, etc.) and finally to grids using county-to-grid areal relationships (U.S. EPA 1989b). Accordingly, for those SCC's applicable to the toxics inventory, county level base quantities for U.S. area sources were determined by back calculating from the reported emissions using a NAPAP emission factor for a selected criteria pollutant (i.e., dividing the emission rate by the emission factor). After converting from Imperial to metric units and assigning appropriate sector codes to cross reference between Canadian and U.S. SCC codes, county-level base quantities were re-assigned to the polarstereographic 127 X 127 km grid system using county centroids. Essentially, this was done for each of the criteria pollutants in order to ensure that back-calculated base quantities matched. In most instances, the relevant NOx emission factors were used as surrogates since NOx emissions are unaffected by fuel sulphur and ash content. In some cases, particulate emission surrogates were also applicable. For most Canadian area sources, in provinces other than Ontario, only emissions data were provided to NAPAP by SCC at the provincial level with gridding

surrogates. Thus, base quantities were back-calculated in an identical manner except that specific Canadian (Environment Canada 1983b) or AP-42 (U.S. EPA 1985) criteria pollutant emission factors were used to correspond with Canadian emissions data. Calculated base quantities were re-assigned to 127 km grids using selected spatial apportioning factors in the Canadian 20 X 20 km gridding surrogate file provided by Environment Canada. On the other hand, most Ontario point and area source base quantity data for 1985 were obtained from the Ontario Ministry of the Environment on the variably-sized UTM grid system and were applied directly in this study. Base quantity grid apportioning surrogates were developed in earlier MOE NOx and VOC studies (ORF/MEP 1983, EAG 1984). In addition, 1985 provincial base quantity information was procured in the present study and consolidated for most of the sectors from Statistics Canada annual, quarterly or monthly reports or other federal/provincial documents. These production, fuel consumption and registration statistics were reviewed as a means to verify the accuracy of the back-calculated and other Canadian base quantities.

In some instances, base quantities required modification or further disaggregation to be compatible with assembled toxic chemical emission factor data (where considered important). Similarly, some activity data were generated for specific non-traditional sources (i.e. those not included in criteria pollutant inventories) using available information. For certain other sources, there was inadequate data to derive or grid base quantities. As an example of base quantity modifications, highway vehicle data were further apportioned by type of catalysts used in gasoline vehicles in order to reflect the impact on toxic emissions. Similarly, residential woodburning base quantities were disaggregated into consumption by woodstoves, fireplaces and furnaces (where possible) since emission rates differ substantially by type of device. Using specific Ontario information, an estimate was made of the amount of black liquor combusted in Kraft pulp recovery furnaces for other geographical areas. Similarly, landfill activity data was estimated and leakage from stored

transformers and other electrical equipment was derived from available Ontario and Canadian storage statistics and estimated for the U.S.

A significant amount of information was also consolidated and assimilated with which to derive pesticide emissions (e.g. available and estimated consumption data for various regions, physical/chemical property data, climatological data as well as specific crop and application method information).

Detailed data on the pesticide useage in both Canada and the U.S. are not generally available and special methods had to be used in Canada to speciate pesticide groups outside of Ontario (herbicides, insecticides, fungicides and nematocides) into individual compounds. Use data for a limited number of individual pesticides were available for the U.S. by state. In the case of pesticides in which use has been discontinued, potential application rates of any remaining 'in-stock' materials could not be estimated.

Details on the use and availability of base quantity data are provided in the sector method descriptions of the text. The special methods used to derive and grid pesticide application rate data are presented in Section 8. As can be seen in Table 3.1.1, specific base quantity information is also lacking for a number of sectors included in the inventory (i.e. especially Canadian waste incineration and open burning data) along with other known and potential sources of these toxic chemicals (see Section 3.11).

3.6 Emission Factor/Algorithm Development

One of the more challenging aspects of the study has been to define or develop chemically speciated emission factors/algorithms that are appropriate to specific sources. This is particularly the case for estimating emissions for several of the important open sources such as pesticide application, volatilization from soils and landfill emissions since these depend on factors such as the actual presence of the toxic on-site, vapour pressures and specific physical/chemical data, the geometry of the area and relevant meteorological conditions. In some instances, upper limit emission factors or algorithms needed to be derived or estimated. The acceptable extent of estimation where data were limited required decisions as the study proceeded (see Section 3.11).

Specific emission factors have been consolidated or derived in this study from reported emission factors, stack measurements or other data. In circumstances where a series of measurements have been done on similar sources, consideration has been given to the reliability of measurements used to derive an average value and caution was used in deleting outlier results that may or may not reflect upset conditions. Preference was given to data in which both vapour and particle phases of the target compounds were reported. However, in several instances, data were available for a limited number of measurements or for only one or two sources that were assigned to represent the sector. In many instances, large variations in measured data were evident, target species were not necessarily common between measurements, and the detection limits (where reported) often could be expected to differ between measurements and/or investigations. Where results were reported as non-detectable, a zero value was assigned and included in the inventory. Emission factor limitations are discussed in Section 3.11. Despite such limitations, sufficient data were available for several of the important anthropogenic point and area sources (e.g.

combustion, incineration, mobile sources) with which to derive a preliminary emission inventory of these chemicals.

The primary information source used for many sectors was a recent study conducted for Environment Canada and the Ontario Ministry of the Environment and reports therein (Johnson 1988) along with additional reports that were subsequently acquired. In that study, emission factors were consolidated for the toxic chemicals of interest based on Canadian source test measurements and other reported emission factors, mainly from U.S. studies. However, efforts were required to consolidate Canadian and other reported emission factors into averages by source type. Where emission measurement data existed for Ontario, source-specific information has often been used to represent emissions of the particular point source. For areas outside of Ontario, average emission factors were used after combining Ontario data. In addition, speciated emission factors were expanded to both existing and some other types of sources where direct emission measurements were lacking. For example, emission factors were sometimes estimated based on other surrogate data (e.g. ash chemical composition in conjunction with reported total particulate emission factors, speciated industrial hygiene measurements, estimated emission composition from unquantified or grouped species profiles using similar sources or downwind measurement data, direct application of emission factors for a given source type to other similar sources). It was recognized that uncertainties increased with the use of surrogate information and the degree of estimation depended on the availability of appropriate data considered to be representative of the unmeasured source. After estimating and ranking relative source strengths in Ontario for these toxics, emphasis was directed toward developing and refining emission factors and algorithms for the strongest contributing sources such as: residential wood combustion, pesticide application, coal combustion, metallurgical coke combustion, gasoline/diesel-powered vehicles and municipal refuse incineration.

As noted in earlier sections of the report, individual emission factors were defined (where possible) for each species or congener of a compound class such that 'total' emissions by either species or compound class can be obtained. Thus, for the class of PAH compounds, the sum of the individual pre-defined species (see Table 3.2.1) was calculated as the 'total' of the compound group rather than broadly-defined class that theoretically consists of hundreds of compounds. It should be recognized that the primary data used to derive emission factors occurred in various forms such as:

- the 'total' of the chemical class was reported in primary data but species were not identified. This occurred most frequently for PCBs and less frequently for PAH. When used directly in this study, species other than the pre-defined compounds may be included in calculated 'total' emissions (e.g. mono- and dichlorobiphenyls, naphthalene, etc.).

- only one or very few species are identified in the primary data without a 'total' of the class. This occurred most frequently for the compound B(a)P that is known to represent only a small fraction of the actual total PAH emissions. Despite this underestimate, in a limited number of instances, the 'total' class emissions for the source or sector might be based on a single or a relatively few number of components.

- the primary data contained a greater number of species than included in the class definition for this study. This occurred on a limited number of occasions for PAHs but frequently for the compound naphthalene. Where possible, the 'total' was based on the sum of the pre-defined species and the undesignated species were deleted.

- the primary data contained several of the species of interest. This occurred frequently for several of the compound classes and compounds or congeners were summed to the class 'total'.

Thus, the 'total' PAH emissions compiled in this study can be expected to underestimate the broadly-defined chemical class of PAHs but the total emissions of each species, as based on available data, will be accounted for in this compilation.

The very nature of open sources presents greater emission estimation difficulties than for confined or exhausted emissions since the latter emissions can be more readily sampled and quantified. As a result, very few directly applicable open source emission factors have been reported for these toxic chemicals.

Open source emissions invariably depend on climatological and meteorological parameters and those few site measurements of emissions cannot be generally applied. In order to facilitate the emissions estimate for pesticides, for example, a model-based algorithm has been developed in this study. Using this algorithm, emissions attributable to pesticide application and volatilization from soils can be estimated for a range of pesticides on an equivalent basis, while including some of the more important soil and atmospheric processes. In the case of the Tier 4 dioxin contaminated sites in the U.S., insufficient data are available for estimating dioxin emission from these sources. Nonetheless, an emission factor based on a soil volatilization model has been provided in the report which will permit approximate order-of-magnitude estimates should detailed data on the sites become available. A detailed description of the algorithms are provided in Section 8. Due to the lack of detailed information on open sources, it can be anticipated that such emission estimates will be less accurate than some of the confined-type sources where measurements exist.

3.7 Procedures for Geographical Apportionment and Gridding

An Eastern North American grid network has been developed in other inventories and studies in order to model the dispersion and ground-level impact of emissions in accordance with meteorological influences and weather patterns. The grid, noted as the MOE modelling grid, is shown in Figure 3.7.1. Similarly, a variably-sized UTM grid network (see Figure 3.7.2) has been developed to cover Ontario with smaller sized grids associated with heavier population areas in order to distinguish areas of greater emission strength (ORF/MEP 1983). Geographical apportionment of data to the combined MOE modelling and UTM grids was done in this study using several methods. For example, point source data were readily apportioned to grids using latitude and longitude data for individual sources contained in NAPAP files, area/open sources were apportioned where necessary with spatial allocation factors and some open sources were manually geographically apportioned using topographical maps.

The apportioning methods, developed in earlier studies, are discussed below to provide an indication of the methods used and data that were provided for this study. Area source spatial allocation factors for the 1985 NAPAP inventory were based mainly on those developed for the 1980 inventory, with adjustments and updates where necessary. These factors were used to apportion county-level area source emissions to individual grid cells. After assigning appropriate area source spatial surrogates, comprising population and housing statistics from census data, land use data (e.g. urban, agricultural, forest and land area) from satellite imagery and county-to-grid areal relationships, the surrogates were applied in conjunction with software developed to process most of the U.S. and Canadian area source data (U.S. EPA 1989b). Some additional commercial and industrial labour force surrogates from census data were also used in apportioning Canadian area source emissions data at the provincial level to grids. These NAPAP inventory files, prepared by Alliance Technologies

Corp., were supplied with approval by EPA for the present study. Similarly, in the course of preparing the NOx and VOC inventories for Ontario (ORF/MEP 1983, EAG 1984) on the variable resolution UTM grid, additional spatial surrogate factors and grid/area apportioning relationships along with specific software was developed for allocating base quantity or activity data at either the province or census subdivision level for several types of area sources to individual grid cells. For example, the population number of dwellings and other indicators in each census subdivision (i.e. sub-county level statistics) were used to apportion provincial fuel totals, vehicle distances travelled and other base quantities to grids by the use of gridded overlays on Ontario (1:150,000 scale) topographical maps with UTM co-ordinates. In some instances, the locations and activity levels of actual sources (e.g. traffic counts on specific highways, railways, number of calls in marine ports, areas burned in forest fires) were assigned directly to UTM grids. Provincial 1985 base quantities for Ontario area sources by SCC on the UTM grid were supplied by MOE for this study.

After selecting the appropriate sources for the present study, all relevant Canadian (excluding Ontario) and U.S. point sources by SCC were assigned to the respective 127 X 127 km grids within the MOE modelling grid network by their lat/long co-ordinates (i.e. a point source file created from sources retained within the NAPAP file). U.S. county area source base quantity data by SCC were derived by back calculations (see Section 3.5) and were apportioned by centroid to the MOE modelling grid. Area source distribution for the Canadian provinces (outside Ontario) was done using C + P gridding surrogate files. Ontario point and area source data were already allocated to the UTM grid network .

Pesticide use data in both Ontario and Quebec were available on a water-shed basis. The use patterns on a county-level resolution were also available for Ontario. The watershed and county-level application rates were apportioned to the UTM grids in Ontario, and the 127 km grids in

Quebec, on an area basis. In the Atlantic and Prairie provinces, the data were transposed to the 127 km grid on the basis of agricultural land-use obtained from atlases. In the U.S., the 20 x 20 km agricultural land-use data used by NAPAP was applied for pesticide gridding. Further details of the gridding procedures for open sources are provided in Section 8.

Figure 3.7.1

MOE Modelling Grid

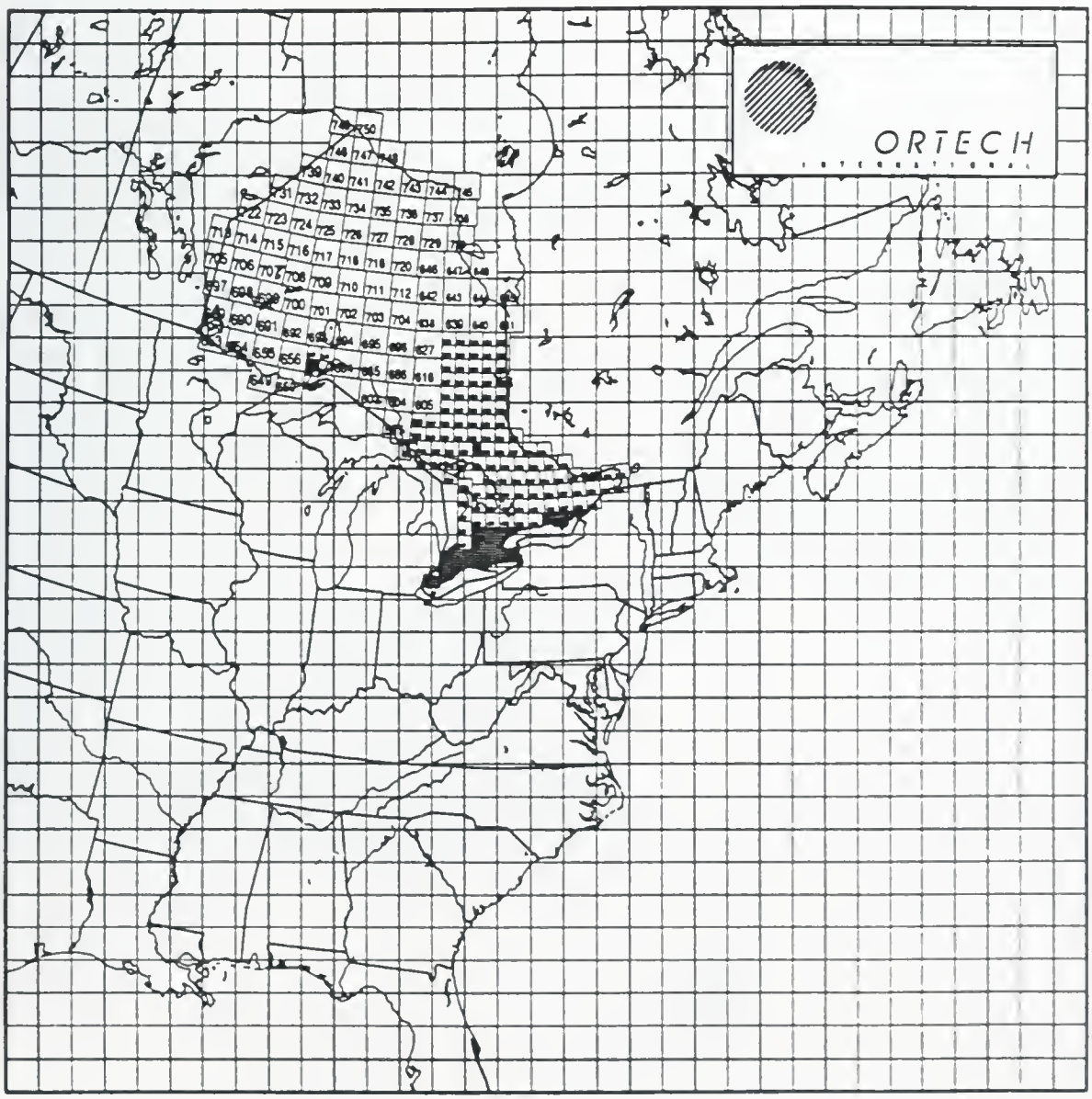
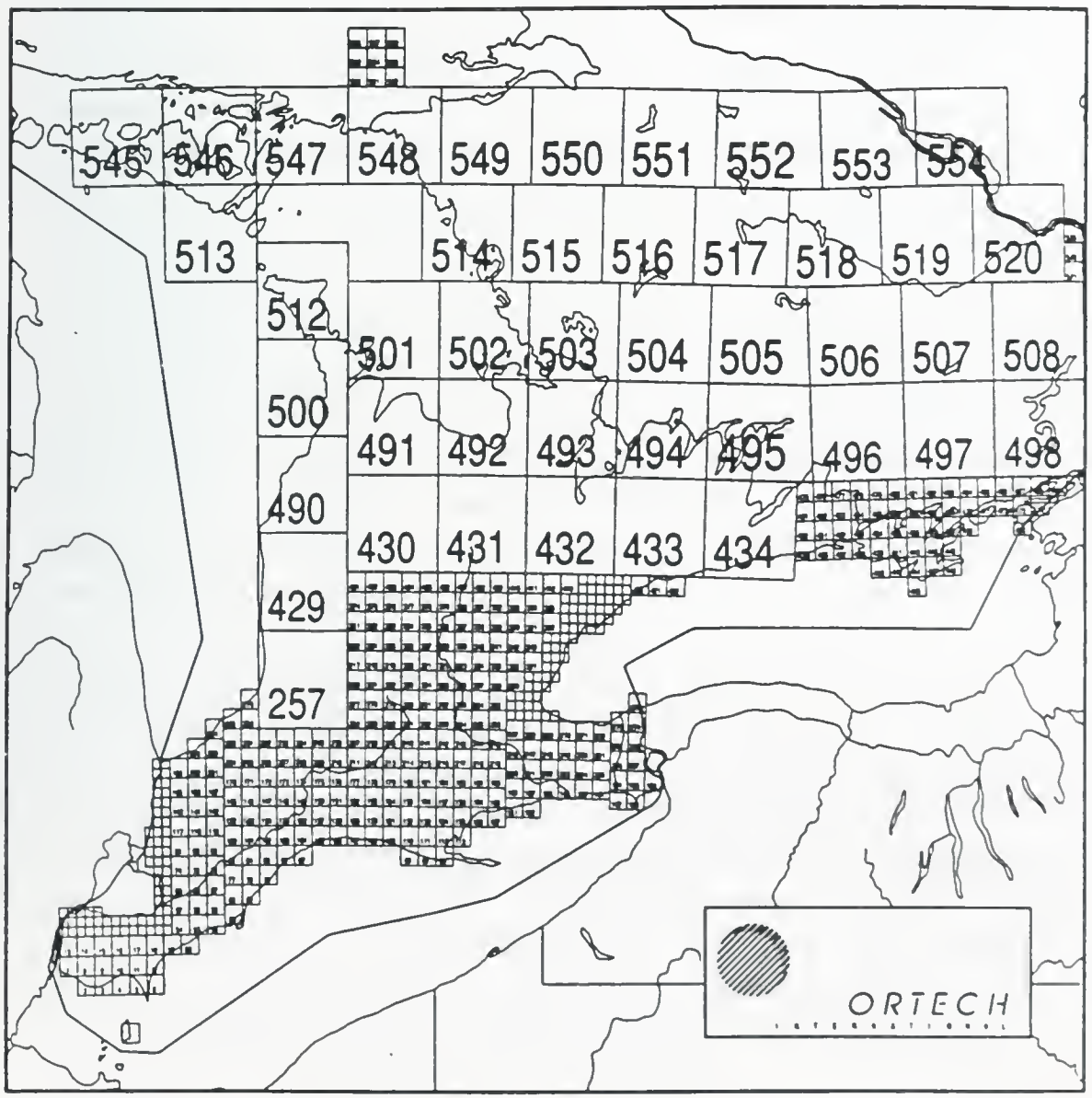


Figure 3.7.2

UTM Grid



3.8 Temporal Factors

For most sources, existing NAPAP data have been used to temporally resolve the annual toxic chemical emissions by season, day-of-week and diurnal periods in order to support modelling applications. For example, in the NAPAP inventory, data were consolidated to allocate annual criteria pollutant emissions by source type into 24 hourly values for a typical weekday, Saturday or Sunday in each of the four seasons of the year (U.S. EPA 1989b). For most point sources, plant- and point-specific operating data were contained in NAPAP files based mainly upon data from previous inventories. For U.S. area sources, many of the temporal factors developed at the state or national level for the 1980 NAPAP inventory were retained or modified somewhat for the 1985 NAPAP inventory while profiles for several new emission source categories were also defined and added. The Canadian point and area source temporal factors were processed in the NAPAP study in much the same manner after conversion to the NAPAP profile format. In addition, Ontario area sources have also been temporally resolved in earlier NOx and VOC inventories to derive UTM grid emission weighted temporal factors (ORF/MEP 1983).

The NAPAP temporal allocation methodology was applied with specific modifications in the current study, on an SCC basis to provide season/day scenarios, each with a diurnal temporal profile (from hour 1 to hour 24) as discussed in Section 9.2.3. The temporal allocation scenarios include: winter weekday, winter Saturday, winter Sunday and a similar allocation for the remaining seasons. It should be noted that the winter season is defined as December through February and that hour 1 corresponds to the period between midnight and 1 a.m. In addition, sector-specific NAPAP temporal factors for Michigan state were applied for area sources in all Canadian provinces.

For pesticide application, the seasonal variability is dominant. There are many seasonal factors which play a role in determining the pesticide emissions such as time of insect infestation, planting, emergence and harvesting of crops, as well as climatological and meteorological factors which determine soil moisture and temperature, for example. The season of pesticide use and mode of application have been estimated based on Ontario Government literature. These estimates, together with the seasonal emission factor estimates, are integrated into a single season factor as described in Section 8.

3.9 Uncertainty Estimation

One of the general responsibilities in compiling emission inventories is to provide an estimate of error or uncertainty of emission data. Various approaches have been taken in determining criteria pollutant emission uncertainties including error propagation methods where data are relatively well-defined. However, a numerical error estimate for a preliminary toxic chemical emission inventory is presently not feasible. In most instances, the largest uncertainties are associated with emission factors and one or more components of algorithms. Some emission factors may vary by an order of magnitude as evident from actual measurements of similar sources. Similarly, large uncertainties may be related to incomplete base quantity data at the required process level. In some instances, only rough estimates are possible in computing emissions. On the other hand, characterization of some toxics released from specific sources is well documented and consistent between studies.

Considerable effort has been directed in this study toward developing an emission algorithm for pesticides which does attempt to include the important physical processes. Nonetheless, the estimates using this algorithm must be regarded as only providing a first estimate. In order to properly model these emissions a more sophisticated time-dependent model would be required. Such modelling work is beyond the scope of the present study.

In this inventory a qualitative rating scheme or uncertainty description has been applied to emission factors and base quantities to reflect the largest source of uncertainty associated with the annual emissions within each sector. Individual ratings are described in Tables 3.9.1 and 3.9.2.

TABLE 3.9.1
Qualitative Base Quantity Accuracy Ratings

Rating	Comment	Description and General Application Criteria
A	Excellent	Based on good quality year-specific data acquired directly from an industry (e.g., questionnaire, annual report, etc.) or other recognized sources of statistical compilation (e.g., Statistics Canada) in which survey data were of known high accuracy or reliability.
B	Good	Based on good quality year-specific information acquired from reports (e.g., source-specific studies which provided process data) or other recognized sources of statistical compilations (e.g., Statistics Canada) in which data were of good reliability.
C	Satisfactory	Based on year-specific reported information (e.g., derived from other inventories or statistical compilations) in which acceptable reliability is known or assumed. In some instances, base quantities may have been back-calculated from available emissions and accepted emission factors to result in reasonably accurate data. In other instances, a process capacity for a given industry may have been used in which the industry or process was known to operate normally.
D	Marginal	Based on reported information or derived from other inventory data. Data may have been derived from other years and assumed to be year-specific or based on industrial capacities in which normal operations were unknown. In some instances, base quantities may have been derived from reported emissions in which the applicability of the emission factor was uncertain.
E	Estimate	Estimate only based on assumptions of operating or activity data or data that have been prorated from other similar information.
N	NAPAP	Base quantities derived or supplied directly from the the 1985 data base in which accuracy cannot be readily assigned.
O	Ontario	Ontario MOE 1985 base quantity data in which accuracy cannot readily be assigned.

TABLE 3.9.2
Qualitative Emission Factor Accuracy Ratings

Rating	Comment	Description and General Application Criteria
A	Excellent	Based on good quality and recent source measurement data acquired under normal process operating conditions. Measurement methods are deemed to be appropriate to the source/pollutant, lack errors and include both vapour and particle phases. Measurements are based on a sufficiently large number of representative or similar sources (e.g., 5 or more) with each source tested at typical operating conditions. Process data to derive a given emission factor is reported with the measurements. Resulting data are consistent between individual sources with which to derive averages and exhibit only minor variability (e.g., variability within a factor of two between all tests).
B	Good	Based on good quality source measurement data obtained under normal process operating conditions. Measurement methods considered to be accurate and include vapour and particle phases. Measurement data are available for typical operating conditions for a few similar sources (e.g., 3 or more) and reported process data are available. Data are generally consistent between individual sources but may exhibit some variability (e.g., variable within a factor of four between all tests).
C	Satisfactory	Based on source measurement data obtained under normal operating conditions in which there is no reason to doubt the accuracy of results. Data may be available for only one or more sources and could be limited to the particle phase only. Data may be variable for multiple tests on a given source or between individual sources and no reason or information can be found to exclude outlier results (e.g., variability may be significant).
D	Marginal	Based on source measurements from only one or more sources in which insufficient data are available to assess the accuracy of measurements. Measurements could be limited to the particle phase only or the phase may not be reported. Measurements may have been taken at atypical operating conditions or may be outdated (e.g., possibility of changed process conditions, changes to control device or efficiencies, questionable or outdated analytical techniques, etc.). No data may be available to assess emission variability or very large data variations may be evident.
E	Estimate	Estimate only based on assumptions of base quantities or other input data due to the lack of direct or appropriate measurements. No information available to assess emission variability.

3.10 Quality Control Procedures

Several quality control procedures were implemented in the study in an effort to compile a reasonably complete inventory and reduce potential errors to the extent possible. At the outset of the study and on specific occasions, general procedures to be used were reviewed with members of a Toxics Committee comprising representatives of both the Ontario and Federal Governments. Similarly, during the conduct of the study, various progress reports addressing procedures and specific data gaps that were found were prepared for Committee review and comment. In addition, because a large portion of the base data for this inventory was developed for the 1985 NAPAP inventory, reports are available to indicate that the data received extensive QA/QC evaluations by U.S. EPA, Environment Canada and the primary contractor-Alliance Technologies Corp. (U.S. EPA 1989b).

For the emission factors developed in this study, data input to the file was reviewed by a designated study team member and values derived for species/congeners were manually summed to ensure equivalence to the reported totals of the compound class.

As noted in Section 3.5, selected area source base quantities by SCC were back calculated from NAPAP emissions data for the U.S. and Canadian provinces outside of Ontario using annual emissions data and emission factors for four criteria pollutants to ensure that back-calculated base quantities were similar. In several instances, the base quantities were similar between pollutants and, when differing, the totals derived for the NOx emission factors were used since NOx emissions would be unaffected by fuel sulphur or ash content and temperature which vary between regions. Once the back-calculated totals were available and all data were converted to metric units, the annual base quantity totals were compared against available 1985 Statistics Canada data on a province and sector basis. Focus was directed toward Canadian data since such statistics were not

compiled for U.S. sources. In most cases, the totals were similar to available statistical data but insufficient time was available to deduce possible reasons for specific inconsistencies. For example, significant efforts would be required to verify the mobile source base quantities due to the rather complex treatment of data. Similarly, the toxic chemical emission totals were calculated manually for many of the sectors using available published statistics and developed 'total' pollutant class emission factors as a means to check computerized totals that would account for errors that could occur for: derived base quantities, unit conversions, emission factor species summation, and data entry. A comparison of the manual and computer generated (back calculated) totals of PAH emissions for various Canadian area source sectors is presented in Table 3.10.1. It can be seen that in most instances emission totals were similar and that generally only minor differences occurred.

Furthermore, in handling NAPAP point source data, the total number of Canadian point sources outside of Ontario for selected sectors to be inventoried (i.e., after excluding non-contributing sources from the NAPAP files) was checked on a provincial basis to ensure that contributing plants were not inadvertently deleted from the file. This was done using previous Canadian inventory information with respect to the anticipated number of Canadian plants rather than point sources. However, insufficient data were available to fully ascertain whether or not individual points might be missing from the data base due to uncertainties in some SCC correspondences but most major sources have been included. One potential discrepancy occurred for aluminum producing facilities in Quebec as noted in Section 11 of the report.

Lastly, the graphical output of the inventory was examined and reviewed by pollutant type to ensure that major point sources were properly located and that distribution patterns of area source contributions appeared reasonable especially for Ontario data. It was evident that the emission distribution

patterns for several of these toxic chemicals were generally similar to the NOx emission distributions for Eastern North America reported in the NAPAP inventory.

TABLE 3.10.1

Comparison of Estimated PAH Emissions (kg) for Various Area Sources in Gridded Canadian Provinces (excluding Ontario) Using Derived and Statistical Base Quantities

Category/Sector			Estimated from Available Statistics[1]	Estimated from NAPAP Back Calculated Base Quantities[2]
Stationary Fuel Combustion				
Electric Power	-	Bit. Coal	481	245
	-	Lignite	67	34
	-	Resid. Oil	<1	<1
Indust. Fuel Comb.	-	Bit. Coal	298	244
	-	Resid. Oil	26	31
	-	Nat. Gas	4,272	4,811
Comm. Fuel Comb.	-	Bit. Coal	237	57
	-	Resid. Oil	5	6
	-	Dist. Oil	<1	<1
	-	Nat. Gas	287	127
Resid. Fuel Comb.	-	Bit. Coal	4,991	4,909
	-	Dist. Oil	2,572	2,491
	-	Nat. Gas	785	232
Resid. Wood Comb.			276,800	357,900
Int. Comb. Diesel Eng.			26	15
Transportation				
Railroads			364	165
Marine			199	68
Solid Waste Incineration				
Munic. Waste Incin.			1,204	1,369
Comm./Inst. Waste Incin.			544	805
Wigwam Burners			18,700	26,950
Open Sources				
Forest Fires & Prescribed Burning			326,800	344,700

Notes: 1. Base quantities summed by province from 1985 Statistics Canada and other reports (includes all of Saskatchewan but excludes Ontario). Sector-specific emission factors were used to estimate emissions.

2. Derived base quantities (see text) for provincial areas within modelling grid (excluding part of Saskatchewan and Ontario). Some sector total emissions contain combined SCC contributions with SCC-specific emission factors.

3.11 Data Gaps and Limitations

As discussed in various sector descriptions and further in Section 11 of the report, pertaining to inventory results, several data gaps, deficiencies and uncertainties have been identified in this study. Limitations occurred for both base quantity data and emission factors. For example, Canadian base quantity data and provincial allocations are lacking for several types of non-traditional sources that can be expected to contribute toxic emissions. Major sources of concern include: wood preservation plants in which open evaporator pans may emit PAH and PCDD, industrial waste incineration regarding PCDD and PCDF emissions and the practice of used railway tie burning that might emit PCDD. Accordingly, only rough estimates can presently be made for these and other potentially minor sources (see Section 10).

As noted in a previous report (Johnson 1988), it should be recognized that many of the emission factors consolidated in this study are based on limited source measurement data that have been reported. In some instances, Canadian measurement data have been combined with U.S. data to generate average emission factors for a particular type of source or sometimes only one measurement from a single source has been available to represent an entire sector. Various measurement techniques have been used which can differ in detection limits for given compounds, methods of data normalization and general validity. In some cases, concentrations of contaminants to be measured may be emitted at trace levels and near detection limits of some measurement methods which can introduce errors in compilation. Similarly, normalization of stack gas volumes to standard or common conditions for combustion sources (e.g. temperature, % oxygen and % carbon dioxide) may not be consistent between measurements which can lead to anomalies when comparing results of different measurements. No efforts have been made in this study to correct reported concentrations or derived emission factors to a consistent set of conditions. Furthermore, there

may be uncertainties in collection efficiencies or analytical recoveries for some components in the various types of sample collection media used for measurements (e.g. filters, impingers, solid adsorbents, etc.) which can cause uncertainties in the resulting emission factors. However, in most instances, more recent measurement data have been used in which a greater degree of validity might be expected than for earlier measurements. It is also important to note that combustion conditions and other specific factors can affect the vapour/particle distribution of semi-volatile species emissions which may vary substantially between source types. The distribution from a predominantly vapour phase to the particle phase for some species may also change rapidly during or after the point of emission due to condensation or adsorption on emitted particulate matter. Moreover, sampling conditions may alter the phase distribution which would present difficulties in attempting to quantify vapour/particle fractions emitted. Although it was not always possible, measurements which included both the vapour and particle phase were given preference in consolidating and deriving emission factors.

There are several types of sources in which emissions of the components of interest might be anticipated but emissions have either not been measured or have been measured at very few sources within a sector. Where adequate data were completely lacking, no attempt was made to quantify emissions in the inventory. Such quantifications, in the absence of data, would be highly speculative and of little utility. However, some sources with such severely limited data have been noted as potential emitters for consideration in future work when more data become available (see Section 11). Some of the semi-volatile organic chemicals addressed here are perceived to form during combustion processes and sometimes in the presence of feed precursors. Emissions may therefore be more dependent on operational practices, combustion conditions and types of control devices used rather than specific dependence on feed or fuel composition. This limits the potential use of deriving emission factors by a mass balance

approach. In addition, because combustion conditions and practices can vary widely between even similar types of facilities, it can be expected that significant variations of emissions can occur. This is demonstrated in the wide range of emission factors reported for some constituents as shown in another report (Johnson 1988). Thus, when a large range of emissions is encountered for a specific facility or between similar facilities, greater uncertainties will result in determining an average emission factor for application to a given source type. Unlike emission factors that have been derived for specific criteria pollutants where more data are usually available, greater uncertainties are associated with the emission factors for many (e.g. SO_2, particulate emissions, etc.) toxic chemicals due to data limitations, emission variability and the inherent uncertainties in quantifying trace or low-level organics in emissions. Accordingly, larger errors might be expected in the emission compilations for these species than for criteria pollutants. In addition, there are limitations associated with defining pollutant class 'total' emissions for these compounds and these have been discussed in Section 3.6 of the report. Hence, the emission factors consolidated and reported in the sections that follow have provided an indication or starting point in determining emission rates of selected compounds for specific sources. Examination, comparison and integration of more data would be required in order to prepare a more accurate and comprehensive toxic chemical inventory of these species.

4. ESTIMATION OF INDUSTRIAL SOURCE EMISSIONS

4.1 Metallurgical Coke Production

4.1.1 Process Description

Coke oven emissions, comprising numerous toxic constituents including PAH, are a combination of gaseous and particulate material resulting from the destructive distillation of coal during coke production. Earlier estimates of B(a)P emissions in Ontario indicated that coke ovens were the dominant industrial source (i.e., contributing ~63%) (MOE 1979). Coking emissions were estimated to represent ~7% of total PAH emissions in the U.S., based upon two U.S. inventories (NRCC 1983). These data suggest that metallurgical coke production represents a particularly strong source of PAH emissions.

In North America, most metallurgical coke is produced by integrated iron and steel industries (i.e., almost entirely by the slot oven process) which accounted for approximately 92% of the total U.S. coke production in 1984 (U.S. EPA 1987a). It is usually produced by heating in a series of adjacent, rectangular, slot ovens arranged in parallel batteries (10-100 ovens/battery and 1-12 batteries/plant) by expelling the volatile constituents of coal which constitute 20-25% of the initial coal charge (IARC 1984, White et al 1975). Approximately 69% coke yield from coal is common.

In the process, as described in detail elsewhere (Parsons 1977, U.S. EPA 1981a, 1987a and c), pulverized and blended coal is cyclically loaded to a series of hot battery ovens by larry cars above the charging ports and each oven is charged within ~10 seconds. Off-gases during charging are generally contained by a collecting main in conjunction with a steam-jet aspirator. After levelling coal peaks in the oven and heating with regenerated gases, the coal is thermally distilled at 900 to 1100°C, typically

for 15 to 18 hours, to produce blast furnace coke and 25 to 30 hours to produce foundry coke. A positive back pressure is maintained to prevent air infiltration and door seals are used to minimize leakage from the ovens. At integrated plants, process gases that evolve during coking are ducted to the by-product plant for recovery of tars, oils and other constituents of the raw coke oven gas. At the end of the cycle, hot coke is pushed from side doors of the ovens to quench cars, deluged with water at the quench tower located at the end of the batteries and finally crushed for use. Fresh quench water may be used, as is done at Canadian plants (Greenfield 1989) and, at some facilities, contaminated or partially contaminated makeup water may be used to quench coke. Although operations are cyclical for individual ovens, by-product yield is essentially continuous due to the large number of ovens within each battery. At many plants, thousands of tonnes of coal per day are processed into coke and coke by-products and up to 30 ovens may be pushed per shift. Travelling hoods or enclosed coke side sheds along the batteries are used for fugitive emission control at most plants. The sheds contain off-gases from coke pushing or door leaks from only the pushing side of the battery. Emission leakage through various oven doors is normally controlled by luting, patching or other door seal mechanisms.

Both particulate and gaseous emissions can be expected to occur from operations or sources such as coal charging, oven door leaks, topside port leaks, coke pushing, coke quenching, battery stacks, tar processing, ammonia processing and the final COG cooling/naphthalene separation process. Various emission control techniques have been described (U.S. EPA 1981a, 1987a and c). Fumes emitted from doors and ports, containing tars in the respirable size range, are reported to consist of ~10% PAH with a large methyl, ethyl substitution fraction (White et al 1975). Because several of the release points are fugitive, cyclical and transient in nature, it is extremely difficult to collect representative samples with which to characterize coke oven emissions. Similarly, emissions from coking operations are highly variable between plants and within processes at the same plant. For

qualitative measurements of such emissions have been done at one creosole evaporation tank facility in Ontario (Konasewich and Henning 1988). Similarly, as shown in Tables 4.7.1 and 4.7.2, both process and evaporator pan emissions of various PAH species have been characterized at specific U.S. facilities (NATICH 1988, DaRos et al 1982). Due to the fugitive nature of such emissions, and the lack of process information during the test programs, it was not possible to express emission rates in appropriate process units.

4.7.3 Inventory Comments

A list of Canadian wood treating plants was obtained from the Department of Regional Economic Expansion (McKellar 1988). This list included some limited information on the chemicals and major treatment methods used by each facility, but no information on operation or production rates. A similar list was available for U.S. preserving plants (Micklewright 1988).

A review of the Ontario data indicated that out of 18 facilities, there were approximately 37 cylinders. Of these, 31 used CCA (Chromated Copper Arsenate), 3 PCP and 3 creosote. Assuming that the PCP and creosote cylinders were run year-round, that the process emissions listed in Tables 4.7.1 and 4.7.2 occur one one hour per day, and that each cylinder has a thermal evaporater pan for wastewater treatment (an extremely conservative assumption), annual emissions of PAH would be estimated at 25 tonnes. This emission estimate is, however, very tentative since both the emission factors and activity levels are in themselves so tentative. Therefore, this sector was not included in the inventory at this time.

TABLE 4.7.1

PAH Emission Factors for Wood Preservation: Creosote Treatment

Source	Compound	Emission Factor
Process[1] Emissions	Acenaphthene	2,600,000 mg/hr
	Acenaphthylene	59,000 mg/hr
	Anthracene	5,000 mg/hr
	Fluoranthene	20,000 mg/hr
	Fluorene	350,000 mg/hr
	Phenanthrene	310,000 mg/hr
	Pyrene	9,000 mg/hr
Evaporator[2] Pan Emissions	Acenaphthene	220,000 mg/day
	Anthracene	370,000 mg/day
	Benz(a)anthracene	7,000 mg/day
	Benzo(a)pyrene	<2,000 mg/day
	Benzo(ghi)perylene	<400 mg/day
	Benzofluoranthenes	4,000 mg/day
	Chrysene	6,000 mg/day
	Dibenzo(ah)anthracene	<400 mg/day
	Fluoranthene	170,000 mg/day
	Fluorene	3,000,000 mg/day
	Indeno(1,2,3-cd)pyrene	<400 mg/day
	Phenanthrene	1,400,000 mg/day
	Pyrene	110,000 mg/day

Notes

1. NATICH 1988. Results for one facility. Includes sum of emissions from vacuum pump exhaust during initial conditioning, final vacuum and opening retort door at the end of the cycle.

2. DaRos et al 1982. Results for one facility. Emissions were from the vent of the thermal pan evaporator for wastewater treatment.

TABLE 4.7.2

PAH Emission Factors for Wood Preservation: PCP Treatment

Source	Compound	Emission Factor
Process[1] Emissions	Acenaphthene	30,000 mg/hr
	Fluorene	20,000 mg/hr
	Phenanthrene	6,000 mg/hr
Evaporator[2] Pan Emissions	Acenaphthene	600,000 mg/day
	Anthracene	1,800,000 mg/day
	Benz(a)anthracene	400,000 mg/day
	Benzo(a)pyrene	<30,000 mg/day
	Benzo(ghi)perylene	<30,000 mg/day
	Benzofluoranthenes	60,000 mg/day
	Chrysene	360,000 mg/day
	Dibenzo(ah)anthracene	<30,000 mg/day
	Fluoranthene	1,000,000 mg/day
	Fluorene	3,600,000 mg/day
	Indeno(1,2,3-cd)pyrene	<30,000 mg/day
	Phenanthrene	3,000,000 mg/day
	Pyrene	3,000,000 mg/day

Notes

1. NATICH 1988. Results for one facility. Includes sum of emissions from vacuum pump exhaust during final vacuum and opening the retort door at the end of the cycle.

2. DaRos et al 1982. Results for one facility. Emissions were from the vent of the thermal pan evaporator for wastewater treatment.

4.8 Carbon Black Manufacture

4.8.1 Process Description

Carbon black, a finely divided carbon produced by the thermal decomposition of hydrocarbons, is a major industrial chemical used primarily as a reinforcing agent in rubber compounds, especially tires. Two types of processes are used in carbon black production: thermal and oil-furnace. In Canada there is one of each type of facility; in the U.S. over 90% of domestically-produced carbon black is via the oil-furnace process. (Serth and Hughes 1980)

In the oil-furnace process, an atomized liquid carbon feed (e.g., highly aromatic petroleum oil) is pyrolyzed in a furnace by heat supplied from combustion with natural gas and air. The suspended carbon black is quenched by water spray at the furnace outlet and collected in bag filters. A portion of the baghouse effluent stream may be returned for product drying but most is vented to the atmosphere. A flame or incinerator may be used after the baghouse in some plants for contaminant control. The raw carbon black collected in the bag filter unit then undergoes further processing, such as pulverizing, drying, pelletizing and packaging. (Serth and Hughes 1980, U.S. EPA 1987a)

Carbon black is also produced less extensively by thermal decomposition of natural gas or exothermic decomposition of acetylene. (U.S. EPA 1987a)

4.8.2 Emission Factors

Both gas and vapour phase PAH compounds have been measured at the (uncontrolled) main process vent (product recovery baghouse) of a U.S. oil-furnace carbon black plant. Table 4.8.1 lists the average emission factors over three tests. The range represents one standard deviation of the mean,

as detailed results were not presented by the authors (Serth and Hughes 1980). Total PAH emission factors have also been reported for other oil furnace facilities with a lesser degree of speciation but consisting of similar characteristic compounds (Siebert 1978 and Miller and Barrett 1975 as cited in U.S. EPA 1987a).

AP-42 (U.S. EPA 1985) states that in the thermal process POM and organic compound emissions from the process vent are negligible because low sulfur natural gas is used and the process offgas is used as fuel.

No emissions data of any type was identified for raw product processing steps such as grinding, drying and packaging. However, Nishioka et al (1986) reported on PAHs identified in a carbon black sample produced via the oil-furnace process (Table 4.8.2). Assuming that all fugitive particulate released from raw-product processing is carbon black, this data can be combined with a total particulate emission rate of .45 kg/tonne carbon black produced (U.S. EPA 1987b) to estimate PAH emissions from this part of the process, which is common to both the thermal and oil-furnace processes.

The oil furnace has an additional reported fugitive particulate emission rate of .08 kg/tonne carbon black produced (U.S. EPA 1987b).

Table 4.8.3 presents the overall PAH emission factor for carbon black manufacture using the oil-furnace method. These emission factors are based on data presented in Tables 4.8.1 and 4.8.2.

4.8.3 Inventory Comments

The PAH emission factors discussed above were applied to points in the MOE (point) inventory and NAPAP (point) inventory (remainder of Canada and the U.S.) for SCC 301005-03 (Carbon Black furnace process gas-main vent) and SCC 301005-04 (carbon black furnace process oil-main vent).

SCC 301005-03 was assigned to MSC 10701 and SCC 301005-04 was assigned to MSC 10702.

TABLE 4.8.1

PAHs Emission Factors for an Uncontrolled Main Process Vent of an Oil Furnace Carbon Black Plant*

	Emission Factor** (mg/tonne carbon black produced)
Acenaphthylene	800 ± 456
Anthracene/phenanthrene	70 ± 48
Benz(a)anthracene/chrysene	9 ± 2
Benzofluoranthenes	30 ± 15
Benzo(ghi)perylenes/anthracenes	23 ± 12
Benzopyrenes/perylene	30 ± 15
Dibenz(ah)anthracene	ND
Dibenzo(cg)carbazole	ND
Dibenzothiophene	14 ± 10
Fluoranthene	60 ± 40
Indeno(1,2,3-cd)pyrene	ND
Methylanthracenes/phenanthrenes	100 ± 40
Pyrene	500 ± 240

* Serth and Hughes 1980
** Range given is one standard deviation

TABLE 4.8.2

Polycyclic Aromatic Hydrocarbons Identified in Carbon Black - Derivation of Total Raw Processing & Fugitive Emission Factors (Nishioka et al 1986)

Compound	Carbon Black µg/g	mg/tonne Carbon Black Thermal**	Oil-furnace***
anthracene	N.D.	0	0
benz(a)anthracene	10	4.5	5.3
benzo(ghi)fluoranthene	60	27	32
benzo(j)fluoranthene	20	9.0	11
benzo(k)fluoranthene	40	18	21
benzo(a)fluorene	N.D.	0	0
benzo(ghi)perylene	*		
benzo(a)pyrene	250	110	130
benzo(e)pyrene	190	86	100
chrysene	20	9.0	11
coronene	*		
cyclopenta(cd)pyrene	70	32	37
dibenzo(def,mno)chrysene	*		
dibenzothiophene	50	23	27
fluorene	N.D.	0	0
fluoranthene	310	140	470
indeno(1,2,3-cd)pyrene	*		
methylanthracenes	N.D.	0	0
methyl phenanthrenes	N.D.	0	0
perylene	120	54	64
phenanthrene	110	50	58
pyrene	570	260	300
triphenylene	1	.5	.5
dibenzofuran	N.D.	0	0

* these compounds were known to be present but were not eluted under the chromatographic conditions used for carbon black analysis.

** total particulate emissions from: transport air vent, drying and bagging/loading = .45 kg/tonne (U.S. EPA 1987b).

*** total particulate emissions from transport air vent, pellet drying, bagging and loading and furnace process (fugitive) =.53 kg/tonne (U.S.EPA 1987b).

TABLE 4.8.3

Total PAH Emission Factors for Carbon Black Production in an Oil Furnace (mg/tonne carbon black produced)

	Emission Factors
Acenapthylene	800
Anthracene	0
Benz(a)anthracene	8.3
Benzofluoranthenes	94
Benzo(a)pyrene	143
Benzo(e)pyrene	110
Chrysene	17
Cyclopenta(cd)pyrene	37
Dibenzo(ah)anthracene	0
Dibenzo(cg)carbazole	0
Dibenzothiophene	41
Fluorene	0
Fluoranthene	530
Indeno(1,2,3-cd)pyrene	0
Methylanthracenes/Methylphenanthrenes	100
Perylene	71
Phenanthrene	128
Pyrene	800
Triphenylene	.5

4.9 Wood Charcoal Production

4.9.1 Process Description

Charcoal is the product of pyrolysis of carbonaceous raw materials. The principal raw materials are medium to dense hardwoods; softwoods, sawdust, nutshells, fruit pits and vegetable wastes are also used (U.S. EPA 1987a).

A typical charcoal manufacturing process consists of four steps:

1. a heating cycle (to 100°C) during which water and highly volatile hycrocarbons are distilled off. After the moisture is drawn off the wood temperature begins to climb.

2. the temperature begins to climb again to about 275°C, and the hydrocarbon distillate yield increases.

3. at about 275°C, externally supplied heat is no longer required as the carbonization reaction becomes exothermic. The wood temperature rises to about 350°C. The bulk of hydrocarbon distillates are produced during this stage.

4. as the exothermic pyrolysis ends heat is again applied, raising the temperature to 400 - 500°C to remove more of the less volatile, tarry materials from the product. It is during this stage that the most potential for PAH formation exists (U.S. EPA 1987a).

Charcoal manufacturing can be classified into either batch (45 percent of U.S. production) or continuous (55 percent of U.S. production).

The Missouri-type kiln is the most common type of batch process. This small kiln, which is often of concrete construction, typically produces 16 tonnes of charcoal over a three week cycle. During manual loading, easily combustible materials are placed at the bottom centre of the kiln. These materials are then ignited in conditions providing the amount of air necessary for rapid consumption of the starting fuels. Air may be supplied through groundline ports in the side walls, auxiliary ceiling ports or through stacks. The air ports are used to control temperatures throughout the cycle. When pyrolysis is complete, the air ports are sealed to start the cooling cycle. Stacks are sealed from 1 to 2 hours later (U.S. EPA 1987a, U.S. EPA 1985)

Pyrolysis typically takes 5 to 8 days of the total cycle. The actual time and resulting emissions vary with the kiln capacity, operational practices, wood type and wood moisture content (U.S. EPA 1987a).

Emissions control from batch type kilns is difficult because of the cyclic nature of the process, resulting in emission composition and flow rate changes throughout the cycle. Batch kilns typically do not have emissions controls, although some may use afterburners for the destruction of hydrocarbons. However, the economics of these typical small batch kilns prohibits the installation of these devices (U.S. EPA 1987a, U.S. EPA 1985).

Hereshoff multiple hearth furnaces are used for continuous charcoal production, averaging 2.5 tonnes of charcoal per hour. In these furnaces, material feed at the top of the furnace moves alternately across the multiple hearths at increasing temperatures until it discharges from the floor of the bottom hearth. It is then cooled by water sprays. Initial heat is provided by oil or gas-fired burners at the sides of the hearths. When the furnace temperature is reached, auxiliary heating stops and combustion air is used to ignite the wood gases to maintain furnace temperature. Auxiliary heating is usually only required for start-up or upset conditions. Exhaust gases are vented through stacks on top of the furnace. These furnaces are usually

controlled by direct-fired afterburners, since emission composition and flow rates are more constant (U.S. EPA 1987a, U.S. EPA 1985).

Although briquetting is often associated with both types of facilities, it is not thought to be a significant source of toxics (particulates are the main emission) (U.S. EPA 1985).

4.9.2 Emission Factors

Only one study for a Missouri-type batch kiln was found in the literature. Based on five sampling runs and limited production data, a total POM emission of 3500 mg/tonne of charcoal produced was measured. Benzo(c) phenanthrene, benzo(a)pyrene and "POM-like" material was identified as being present, but was not quantified. Four compounds were analyzed for, but not detected: dibenz(a,h)anthracene; 3-dimethylcholanthrene; 7,12 dimethylbenz(a)anthracene; and 3,4,5,6-dibenzocarbazole. In reporting these results, Kelly (1983) notes that these tests were of questionable value, due to the difficulty of sampling the kiln and the improvisational sampling techniques used.

No other emissions testing was found for batch or continuous wood charcoal production.

4.9.3 Inventory Comments

A total PAH emission factor of 3500 mg/tonne of charcoal produced was used to estimate point sources listed in the MOE NAPAP point inventories under SCC 301006-01,03 and -04. This included "general" batch kiln and continuous charcoal manufacturing processes. No charcoal manufacturing point sources were listed for Ontario in the MOE inventory or the rest of Canada in the NAPAP point source inventory. All PAH emissions were assigned to Master Sector Code 10801.

4.10 Petroleum Refining

4.10.1 Process Description

The petroleum industry converts crude oil into over 2500 refined products. There are five major categories of processes and associated operations: separation processes, petroleum conversion processes, petroleum treating processes, feedstock and product handling, and auxiliary facilities (U.S. EPA 1985). Of these, two categories have been identified as potential sources of PAH. Utility boilers (auxiliary facilities) are discussed in section 5.2. Catalytic cracking units (petroleum conversion processes) have also been found to emit PAHs.

Catalytic cracking increases the production of the lighter, more valuable gasoline and distillate blending products from crude oil. One of the by-products of the cracking process is carbon, in the form of coke. The coke deposits on active sites of the catalyst. Catalyst regeneration units, in which these coke deposits are burned off, are operated to continuously supply fresh catalyst and heat to the cracking process. Normally, off-gases, that contain PAH, are transported to a carbon monoxide waste heat boiler and particulate emissions are further controlled by ESPs or plume burners (U.S. EPA 1987a, Kelly 1983, Johnson 1988).

Three types of catalytic cracking units are used: fluid-bed (FCC), Thermofar (TCC) and Houdriflow (HCC). As of 1979, in the U.S., FCC units represented 94 percent of the total cracking units, with this expected to increase with new catalysts, design and operational changes being developed at that time (Radian 1980 as cited by U.S. EPA 1987a). Of the twenty-eight Canadian catalytic cracking units operating in 1983, twenty-six were FCC units with sixteen having particulate control systems, primarily CO boilers (Grant 1985).

4.10.2 Emission Factors

Hangebrauck et al (1967) measured several PAHs for FCC (controlled and uncontrolled), TCC (controlled) and HCC (controlled and uncontrolled) units. Since the majority of catalytic cracking units are FCC controlled with a CO waste heat boiler, the emission tests for these units are presented in Table 4.10.1. The technique used by Hangebrauck is under some dispute. U.S. EPA (1987a) states in some sections that this series of Hangebrauck tests represents primarily particulate; other sections (such as the petroleum refinery section) state that the techniques used collected both particulate and vaporized PAH.

4.10.3 Inventory Comments

Canadian and U.S. FCC and TCC units were inventoried as point sources as listed in the NAPAP or MOE (Ontario only) point source inventories under SCC's 306002-00 and 306003-01 using the average PAH emission factors listed in Table 4.10.3. All emissions were assigned to Master Sector Code 10901.

TABLE 4.10.1

**PAH Emission Factors for FCC Units
(mg/kl (fresh feed and recycle))***

	Average	Range
Anthracene	ND	-
Benzo(a)pyrene	.092	ND-.18
Benzo(e)pyrene	.11	ND-.18
Benzo(ghi)perylene	.15	ND-.46
Coronene	ND	-
Fluoranthene	.49	.17-.71
Perylene	ND	-
Phenanthrene	.77	.21-1.4
Triphenylene	ND	-

* From Hangebrauck et al 1967. Results are from 3 tests. Samples were only analysed for the PAHs listed.

4.11 Asphalt Roofing Manufacture

4.11.1 Process Description

Asphalt roofing products include asphalt saturated felt rolls, roll roofing with mineral granules on the surface, and smooth roll roofing that may contain a small amount of mineral dust or mica on the surface (U.S. EPA 1987a).

The asphalt roofing manufacturing process can be divided into: (1) asphalt storage, (2) asphalt blowing, (3) felt saturation, (4) coating, and (5) mineral surfacing. If glass fibre is used in place of paper felt, the asphalt saturation step is bypassed.

The saturant and coating asphalts used in the production of asphalt roofing are a processed asphalt flux, which is usually a blend of crude oil residuum from the refining process. Asphalt is prepared for use by blowing air through the heated flux to raise the temperature at which it will soften. A stabilized coating asphalt is then prepared by mixing the blown asphalt and a mineral stabilizer in approximately equal proportions (U.S. EPA 1980). Asphalt flux is sometimes blown by the oil refiner or asphalt processor to meet the roofing manufacturer's specifications. Many roofing manufacturers, however, purchase the flux and carry out their own blowing (U.S. EPA 1980, as cited by U.S. EPA 1987a). Air blown asphalts are also used in the installation of built-up roofs and for the repair of leaky roofs (U.S. EPA 1980).

Asphalt is transferred within a roofing plant by closed pipeline. Barring leaks, the only potential emission sources are the end-points: the storage tanks, the asphalt heaters and the air blowing stills (U.S. EPA 1987a).

In the manufacturing process, felt is fed from a dry looper into the saturator, where moisture is drawn out and the felt fibers and intervening spaces are filled with saturant asphalt. Sometimes spraying may be combined with

dipping at this step. The saturated felt then passes through drying-in drums and onto the wet looper, sometimes called the hot looper. This provides further time for the saturant to penetrate the felt.

If surfaced roofing products are being manufactured, the felt then goes through coating and surfacing steps.

Further details on the asphalt roofing manufacturing processes can be obtained in U.S. EPA 1980 and U.S. EPA 1987a.

Process controls and add-on control devices can be used to reduce emissions from these processes. Process control devices commonly used include: afterburner, high velocity air filter or ESP for the saturator, wet looper and coating steps; a high velocity air filter for the coater-mixer; an afterburner for the asphalt blowing still; and a mist eliminator for the asphalt storage tanks.

4.11.2 Emission Factors

As part of a regulatory standards of performance development program for the asphalt roofing manufacturing industry, the U.S. EPA conducted a source testing program to evaluate techniques for controlling particulate emissions related to processes in the industry. Plant process facilities tested included asphalt storage tanks, blowing stills, saturators and coaters. These tests included sampling and analyses of PAH in particulate. The emission factors presented in Table 4.11.1 are based on these tests. (U.S. EPA 1980)

The asphalt blowing particulate PAH emission factor is based on measurements on two asphalt blowing stills with a capacity of 36.34 m^3 each. Blowing durations were 1 1/2 hours for saturant blows and 4 1/2 hours for coating blows. Each still was equipped with a knock-out chamber followed by an afterburner and heat exchanger. Results presented are for particulates

sampled after the afterburner but before the heat exchanger. (U.S. EPA 1980)

The manufacture/storage particulate PAH emission factors are averages from two facilities tested. The first was a shingle manufacturer with a production rate of 26.31 Mg/h. Sources tested included the spray-dip saturator, dyring-in section, wet looper, coater and asphalt and process storage tanks. Samples were taken at the outlet of a high velocity air filtration (HVAF) unit. The second facility was also a shingle manufacturing plant with a production rate of 28.15 Mg/h over the four tests conducted. Sources tested included a dip-type saturator, drying-in drum section, wet looper and coater. Samples were taken at the outlet of an ESP. (U.S. EPA 1980)

No other speciated PAH measurements were identified.

4.11.3 Inventory Comments

Asphalt blowing PAH emission factors listed in Table 4.11.1 were applied to U.S. point sources in the NAPAP point source inventory listed under 305001-01,02 (asphalt roofing-asphalt blowing) and 306011-01 (petroleum industry-asphalt blowing). Asphalt manufacturing and storage PAH emission factors listed in Table 4.11.1 were applied to Ontario and U.S. point sources in the NAPAP point source inventory listed under 305001-03,04,05 (asphalt roofing-felt saturation). No Canadian point sources were included in the NAPAP for any of these sources. All emissions were assigned to Master Sector Codes 11001 (blowing) and 11002 (manufacture and storage).

TABLE 4.11.1

Particulate PAH Emission Factors for Asphalt Blowing and Asphalt Shingle Manufacture/ Asphalt Storage*

	Asphalt Blowing (mg/tonne asphalt)	Asphalt Storage and Shingle Manufacture (mg/tonne product)	
Anthracene/Phenanthrene**	16.0	44	(24-63)
Benz(a)anthracene/Chrysene***	.82	.61	(.37-.85)
Benzofluoranthenes	.96	.29	(.19-.38)
Benzo(a)pyrene	.33	.2	
Benzo(e)pyrene	.59	.3	
Fluoranthene	1.2	2.3	(1.3-3.3)
Methylanthracenes	not analysed	71	(55-88)
Perylene	N.D.	N.D.	
Pyrene	1.6	2.4	(1.5-3.3)

* Based on U.S. EPA 1980. See text for further details.

** This may be broken down into 3% anthracene, 97% phenanthrene based on analyses of oxidized bitumen in IARC 1985.

*** This may be broken down into 24% benz(a)anthracene and 76% chrysene based on IARC 1985.

4.12 Asphalt Hot Mix

4.12.1 Process Description (U.S. EPA 1987a)

Hot mix asphalt (or asphalt concrete) is produced by heating aggregate to eliminate moisture and then mixing in hot asphalt cement. The aggregate, which is composed of gravel, sand and mineral filler, typically comprises between 90-95% by weight of the asphalt mixture. Asphalt cement is generated as a residue from the distillation of crude petroleum. The resulting hot mixture is pliable and able to be compacted and smoothed. When it cools and hardens, hot mix provides a waterproof and durable pavement for roads, driveways, parking lots and runways.

Recycled hot mix asphalt (removed from existing roads) may also be used in the production of new hot mix asphalt. While the recycled hot mix asphalt may comprise up to 60% of the new asphalt mixture, 25 to 50% is more typical.

There are three main types of hot mix asphalt plants: batch-mix, continuous-mix, and drum-mix. The first two separate the aggregate drying process from the mixing of aggregate with asphalt cement, while drum-mix plants combine these two processes. Production capacities range from 36 to 544 tonnes of hot mix per hour for all three types of plants. In the United States over 80% of all hot mix plants are mobile. More details are available in U.S. EPA 1987a.

4.12.2 Emission Factors

In U.S. EPA 1987a, two studies that evaluated detailed emission factors for PAH are reported. These tests indicated that for drum-mix plants, PAHs are emitted primarily in vapour form (Fuchs et al 1984) and in particulate form for batch plants (Khan et al 1977). The results, which include virgin and recycled feed, drum and batch-mix plants, and different control situations,

were averaged to obtain emission factors for hot mix asphalt production (see Table 4.12.1).

These emission factors do not include an estimate of the PAH emitted during the paving process itself. While some literature was identified on occupational health exposure studies for workers in the paving industry (e.g., IARC 1985), it was not possible to develop an emission factor from this data.

4.12.3 Inventory Comments

Hot mix production PAH emission factors listed in Table 4.12.1 were applied to area sources in Canada (less Ontario) and point sources in Ontario and the U.S.

In Canada, NAPAP area source NAPAP inventory provincial TSP emissions were converted back to base quantities using an emission factor of .137 kg/tonne asphalt (Environment Canada 1983b). Population was used as a spacial allocation surrogate. A default flat temporal factor was used.

In Ontario and the U.S., these sources were inventoried in the MOE and NAPAP and MOE point source inventories (respectively) under SCCs 305002-01 (rotary dryer) and 305002-05 (drum dryer). Fuel use listed under SCC 305002 was assigned to the appropriate industrial fuel combustion category.

Hot mix production emissions in Canada and the U.S. were assigned to Master Sector Code 11101.

TABLE 4.12.1

PAH Emisson Factors for the Production of Hot-Mix Asphalt* (mg/tonne)

PAH	Mean E.F.	Range	# of Measurements
Anthracene	1.7	0.8 - 2.0	4
Benzo(a)pyrene	0.06	ND - 0.13	4
Benzo(e)pyrene	0.16	0.02 - 0.34	4
Benzo(b)fluoranthene	0.04	0.01 - 0.06	4
Benzo(j)fluoranthene	N.D.		4
Benzo(k)fluoranthene	0.06	0.03 - 0.10	4
Benz(a)anthracene	0.11	0.02 - 0.21	4
Benzo(ghi)perylene	N.D.		4
Chrysene	0.54	0.13 - 1.0	4
Dibenz(ah)anthracene	0.3		1
7H-Dibenzo(cg)carbazole	0.3		1
Fluoranthene	1.2	0.3 - 2.3	5
Indeno(1,2,3-cd)pyrene	0.06	0.01 - 0.16	5
Methylanthracenes	0.4		1
Perylene	0.04	0.02 - 0.06	4
Pyrene	2.5	0.8 - 4.2	5
Phenanthrene	15.0	10.0 - 26.0	4

*See text for details

4.13 Kraft Pulp and Paper Production

4.13.1 Source Description

Black liquor recovery furnaces used at Kraft pulp and paper mills to generate steam and recover process chemicals represent potential sources of dioxins, furans and other contaminants. Operations are described in various reports (Ekono 1976, Environment Canada 1979 and 1983a). The concentrated black liquor, containing 60 to70 % solids, is sprayed into the furnace with air control to create both reducing and oxidizing zones within the furnace chamber. Particulate emissions, consisting primarily of sodium sulphate, sodium carbonate and possibly sodium chloride, are normally controlled by electrostatic precipitators. Results have shown that minor amounts of PCDDs and PCDFs, with characteristic patterns, are formed during the bleaching of pulp and that recovery boilers may be a likely source of atmospheric emissions of such constituents (Swanson et al 1988). U.S. data indicate that PCDDs are not formed in the Kraft unbleached pulp processes (Amendola 1987). Sources of chlorine-containing substances in the black liquor include saltcake, from the ClO_2 generator, salt in pulping wood chips, chlorine in ground water used as black liquor makeup water and traces of pentachlorophenol in the feed (U.S. EPA 1987e). In EPA's Tier 4 program, emissions from three facilities have been tested comprising both low-odour and direct recovery boilers. Other sources of PCDD, PCDF and PAH emissions in the pulp and paper industry include dutch oven or other boilers used to burn hogged-fuel or wood waste to produce steam, as well as conical or wigwam bumers to bum wood waste. Dutch oven emissions are discussed in the industrial wood combustion section of the report and emissions from wigwam burners are discussed in the incineration section.

4.13.2 Emission Factors

Average controlled emission factors and ranges for black liquor recovery furnaces are presented in Table 4.13.1. Each facility tested was controlled by an electrostatic precipitator and one used distillate oil as an auxillary fuel. The lowest of these emissions was found at one of the two low-odour recovery boilers which also showed lower total chloride content of the black liquor feed (U.S. EPA 1987e). The original EPA test data were provided in units of µg pollutant/kg of dry solids feed rate which were converted to mg pollutant/tonne air-dried pulp produced in order to correspond with available base quantitiy data. An average conversion factor (i.e., 1.4 tonnes black liquor burned per tonne of Kraft pulp produced) was estimated from the amount of black liquor burned at Ontario plants (i.e., MOE questionnaire data) and the estimated amount of pulp produced at those plants (Johnson 1988). The range of emission factors was based on the lowest and highest result found in three individual test runs at each facility. It is important to note that 2,3,7,8-TCDD was not detected in any of these measurements. This is consistent with measurements conducted at a Swedish recovery boiler (Swanson et al 1988).

TABLE 4.13.1

Emission Factors for Kraft Pulping Recovery Furnace Black Liquor Combustion

Pollutant	Controlled Emission Factor (mg/tonne AD pulp produced)[1]	Range[2]
Total PCDD	0.011	0.0017-0.049
2,3,7,8 T_4CDD	ND	ND
T_4CDD	0.00029	ND-0.0012
P_5CDD	0.00038	ND-0.0025
H_6CDD	0.0011	ND-0.0047
H_7CDD	0.0029	0.00048-0.014
O_8CDD	0.0059	0.0012-0.027
Total PCDF	0.0058	0.00058-0.017
2,3,7,8 T_4CDF	0.000034	ND-0.00018
T_4CDF	0.0013	ND-0.0033
P_5CDF	0.00090	ND-0.0047
H_6CDF	0.0016	ND-0.0051
H_7CDF	0.0015	0.00029-0.0038
O_8CDF	0.00048	0.000096-0.0015

Notes:

1. Emission testing on three separate low odour or direct recovery boilers with or without auxillary fuel (all containing small quantities of PCP in feed) controlled by wet or dry bottom ESP. Original test data, in units of µg pollutant/kg dry solids feed rate, were converted to mg pollutant/tonne air dried pulp produced based on an estimated black liquor generation rate per tonne of pulp produced.

2. Range for individual test runs based on three measurement sets per furnace.

5. STATIONARY FUEL COMBUSTION EMISSIONS

5.1 Electric Power Generation

5.1.1 Source Description

This sector includes the production of electricity with external combustion fossil fuel-fired boilers. The production of electricity through internal combustion units is discussed in Section 5.7.

Table 5.1.1 lists the major combustion systems included in this sector. Distillate oil is not included in this list as it is primarily used for startup and flame stabilization in boilers, and in blending with residual oil to reduce the total sulfur content of the fuel oil consumed. (Shih et al 1980)

In pulverized coal furnaces, pulverized coal with the consistency of talcum powder is generally entrained in primary air before being fed through the burners to the combustion chamber where it is fired in suspension. Pulverized coal furnaces may be classified as either wet bottom or dry bottom, depending on the ash removal technique. Further classifications are based on the firing position of the burners (single front or rear) wall, horizontally opposed, vertical, tangential, turbo or arch fired). (U.S. EPA 1985)

In cyclone furnaces, crushed low ash fusion temperature coal is fed tangentially to a horizontal cylindrical combustion chamber. The finer coal particles burn while in suspension. The coarser particles are thrown to the walls by centrifugal forces. The walls have a surface coating of molten slag which retains most of these coal particles until they are burned. (U.S. EPA 1985, Shih et al 1980)

Mechanical stokers burn coal in fuel beds (as opposed to burning in suspension). All mechanical stokers feed coal onto a grate with provisions for ash removal. The spreader stoker, most common in utility applications, introduces coal into the furnace over the fire bed with a uniform spreading action. Combustion occurs partly in suspension and partly on the grate. Flyash reinjection from mechanical collectors is commonly employed to improve boiler efficiency. Anthracite coal is burned in travelling grate stokers because of the high ignition temperature. In these, coal is fed onto a travelling or vibrating grate and burns as it travels through the furnace. (U.S. EPA 1985, Shih et al 1980)

Oil and natural gas-fired utility boilers have burner arrangements similar to those for pulverized coal-fired utility boilers. Tangential, front wall and horizontally opposed are the primary firing configurations (Shih et al 1980).

Three main types of emissions control are used for utility boiler emissions reduction: boiler modification, fuel substitution and flue gas cleaning. Boiler modification includes any physical change in the unit or its operation. Fuel substitution involves the firing of "cleaner" fuels either by substitution or blending.

Flue gas cleaning on utility boilers is mainly directed at reducing emissions of particulates and sulfur dioxides.

For particulate control, electrostatic precipitators are the most common control for pulverized and cyclones, while multiple cyclones are generally used for stokers and oil-fired units. (Only 20 percent of oil-fired units were estimated to have particulate control in 1976.) Natural gas-fired units do not normally have particulate control. Other particulate control devices include fabric filters (baghouses) and scrubbers. (U.S. EPA 1985, Shih et al 1980)

Flue gas desulphurization (FGD) processes can be wet, semi-dry or dry. Wet systems, the most commonly applied system, generally use alkali slurries as the adsorbent medium. Particulate reduction of up to 99 percent is also possible with wet scrubbers, but flyash is often collected by upstream ESPs or baghouses to increase the efficiencies and lifespan of these units. FGD units are largely used on bituminous and lignite coal-fired units, although some oil-fired units do have these installed. (U.S. EPA 1985, Shih et al 1980)

5.1.2 Emission Factors

PAH emission factors for coal-fired utility boilers are listed in Table 5.1.2. Table 5.1.3 lists PAH emissions factors for other fossil fuel-fired utility boilers.

Emissions of some PAHs have been relatively well investigated for the utility sector. However, because of the various types of firing configurations, control devices, fuel composition and methods of sampling, analyses and reporting, it is sometimes difficult to make appropriate comparisons between reported emission factors or to utilize a sufficient number of sources. From the data availalable, efforts have been made to compile emission factors for the most common types of facilities in use (see Table 5.1.1). However, sufficient data was not available to derive, for any given fuel (and in some cases boiler type), separate emission factors for different firing configurations, process control equipment and operating capacities. Where necessary, factors were converted from energy to fuel consumption units in order to make use of more readily-available fuel consumption statistics. This involved using typical thermal heating values for the various types of fuels and coal types reported in AP-42 (U.S. EPA 1985). Detailed notes in Table 5.1.2 and 5.1.3 provide further information on these PAH emission factors. Although one detailed measurement program on coal-fired stokers indicated no detectable PAH emissions (see Table 5.1.2), several other studies of total POM indicated that stokers had the highest overall POM emission rate. Therefore, bituminous

pulverized dry bottom emission factors were used for bituminous stokers in this inventory. No measurements of distillate oil-fueled utility boilers were identified. Industrial distillate oil boiler PAH emission factors were used for this Sector.

PCB, dioxin and furan emission factors for utility boilers are reported in Table 5.1.4.

5.1.3 Inventory Comments

Based on the literature review discussed in Section 5.1.2, emission factor files (EFF's) were derived as follows:

Fuel, Master Sector Code	EFF's Created	Units
anthracite 20101	EFF's for lignite fueled boilers	mg/tonne
bituminous, sub-bituminous 20102	PAH - pulverized wet bottom - pulverized dry bottom - cyclone - stoker PCDD, PCDF, PCB-all boilers	mg/tonne
lignite 20103	PAH, PCDD, PCDF-all boilers	mg/tonne
residual oil 20104	PAH, PCDD, PCDF-all boilers	mg/kL
distillate oil 20105	PAH - from industrial distillate oil-fired boilers PCDD, PCDF-all boilers	mg/kL
natural gas 20106	PAH, PCDD, PCDF-all boilers	mg/kL
wood 20601	PAH, PCDD, PCDF - industrialwood boilers (See 5.3)	mg/tonne

These were applied to both point (P) and area (A) base quantities obtained from MOE (O) or NAPAP (N) as follows:

Master Sector Code	Ontario	Can. (other)	U.S.
20101	-	-	NP
20102	OP	NP	NP
20103	OP	NP	NP
20104	-	NP,NA	NP
20105	OP	NP,NA	NP
20106	OP	NP	NP
20601	-	-	NP

For point sources, only those with non-zero base quantities were inventoried. All temporal factors were point specific.

For area sources, base quantities for distillate and residual oil were back calculated from annual criteria pollutant emissions using emission factors from AP42 (U.S. EPA 1985). Industrial labour force distribution was used as a spacial allocation surrogate. Emissions from these sources were assumed to be evenly distributed throughout the year.

TABLE 5.1.1

Classification of External Combustion Systems for Electric Power Generation With Predicted U.S. Generating Capacity in 1985 (Shih et al 1980)

Combustion System	Generating Capacity (MW)	% of Total. Gen Capacity	Typical Unit Size (MW)
External Combustion	496,896	100	
Coal	330,826	66.5	
Bituminous	303,210	61.0	
Pulverized dry	251,346		200
Pulverized wet	25,817		120
Cyclone	24,808		250
All stokers	1,239		15
Anthracite	420	<.1	
Pulverized dry	147		235
All stokers	273		10
Lignite	27,196	5.5	
Pulverized dry	25,096		430
Cyclone	1,915		380
All stokers	185		17
Petroleum	103,962	20.9	
Residual Oil	103,962	20.9	
Tangential firing	42,980		270
All Others	60,982		100
Gas	62,108	12.5	
Tangential firing	15,093		200
All Others	47,105		100

TABLE 5.1.2

Average PAH Emission Factors (and Ranges) for Coal-Fired Utility Boilers (mg/tonne)

	Bituminous				Lignite
	Pulverized Dry Bottom	Pulverized Wet Bottom[a]	Cyclone	Stoker[a]	
Anthracene	.85 (ND-2.22) abc	ND	.32 (ND-2.9) a	ND	.17 (ND-.54) ab
Acenaphthene	.29 (ND-.73) bc				ND b
Acenaphthylene	.51 (ND-1.62) bc				ND b
Benz(a)anthracene	.84 (ND-3.02) abc	ND	ND a	ND	.07 (ND-.29 ab
Benzo(b)fluoranthene	.73 (ND-1.73) abc	34.7 (ND-208)		ND	.20 (ND-.93) ab
Benzo(k)fluoranthene	.43 (ND-1.55) abc	ND	ND a	ND	.15 (ND-.69) ab
Benzo(a)fluorene	2.43 (.73-3.9) b				.15 (ND-.24) b
Benzo(ghi)perylene	4.88 (ND-13.8) abc	20.8 (ND-125)	ND a	ND	.89 (ND-3.9) ab
Benzo(a)pyrene	6.58 (ND-48) abc	97.2 (ND-583)		ND	.33 (ND-.95) ab
Benzo(e)pyrene	.13 (ND-.24) ab		ND a	ND	.73 (ND-4.0) ab
Coronene	ND a	ND	ND a	ND	ND a
Chrysene	1.48 (ND - 5.54) abc	108 (ND-647)	.02 (ND-.35) ad	ND	.12 (ND-.54) ab
Dibenz(ah)anthracene	2.3 (ND-6.27) abc		ND a		ND a
Dibenz(ah)acridine					.20 (ND-.36) b
7H-Dibenzo(cg)carbazole					
Fluorene	.69 (ND-2.68) abc	ND	.003 (ND-.003) ad	ND	.07 (ND-.18) ab
Fluoranthene	4.50 (ND-15.5) abc	84.8 (ND-510)	ND a	ND	.14 (ND-.66) ab
Indeno(1,2,3-cd)pyrene	.12 (ND-1.2) bc	31.1 (ND-187)		ND	.32 (ND-.59) b
Methylanthracenes	5.04 (1.0-16.5) b	ND	ND a	ND	.85 (.60-.93) b
Methylphenanthrenes	1.46 (ND-7.1) b		9.44 (ND-56) a		ND a
1-nitropyrene	1.24 (.24-2.3) b				1.6 (.42-2.8) b
Perylene	ND a	ND	ND a	ND	ND a
Phenanthrene	9.38 (ND-31.4) abc	267 (ND-1540)	.22 (ND-5.3) ad	ND	.22 (ND-.93) ab
Pyrene	4.73 (ND-17.0) abc	188 (ND-1130)	ND a	ND	1.4 (ND-6.9) ab
Triphenylene	.05 (ND-.11) ab	ND	NDa	ND	.02 (ND-.05) ab

TABLE 5.1.2 (contd.)

Average PAH Emission Factors (and Ranges) for Coal-Fired Utility Boilers (mg/tonne)

Notes

a Shih et al 1980. Factors represent total of particulate and gaseous PAH. Pulverized bituminous dry bottom: 3 sites were tested (1 scrubber, 2 ESP/multicyclone controlled); 77 to 282 MW operating capacity, 79-100% of base load. Pulverized bituminous wet bottom: 6 sites tested (various pollution control); 110 to 830 MW operating capacity, 86-100% of base load. Bituminous coal cyclone: 11 tests at 6 sites; 119-640 MW operating capacity, 68 - 86% of base load (ESP or scrubber controlled). Bituminous coal stoker: 3 sites tested (baghouse or multicyclone-controlled); 9.9-11.2 MW operating capacity, 78-89% of base load. Lignite-fired utility boilers (multicyclone or ESP controlled): 3 pulverized dry bottom, 20-68 MW operating capacity, 100% of base load; 2 cyclone, 383-420 MW operating capacity, 87-96% of base load; 2 spreader stokers, 7.5-12.3 MW operating capacity, 82-94% of base load.

b Evans et al 1985. Factors represent total of particulate and gaseous PAH. Bituminous dry-bottom: 2 tests each at 2 ESP controlled sites, 150-500 MW operating capacity, full load conditions. Lignite: 2 tests at pulverized dry bottom ESP controlled site, 300 MW operating capacity, 100% of base load.

c Thorndyke 1988. Factors represent total of particulate and gaseous PAH, over a range of low and high load. Facility is a dry bottom pulverized bituminous coal-fed unit with an operating capacity of 500 MW. ESP controlled.

d Haile et al 1983. Factors represent total of particulate and gaseous PAH. 3 cyclone bituminous coal-fired units, ESP controlled, each tested 5 times. Net operating capacities ranged from 150 to 548 MW, 45 to 100% of base load tested.

TABLE 5.1.3

Average PAH Emission Factors (and Ranges) for Natural Gas and Residual Oil-Fired Utility Boilers (mg/kL)

	Natural Gas[a]	Residual Oil
Anthracene	ND	ND ab
Benz(a)anthracene	ND	ND a
Benzo(b)fluoranthene	ND	ND a
Benzo(j)fluoranthene		
Benzo(k)fluoranthene	ND	ND a
Benzo(a)pyrene	ND	.002 (ND-.004) ab
Benzo(e)pyrene	ND	.01 (ND-.02) ab
Benzo(ghi)perylene	ND	.0007 (ND-.002) ab
Chrysene	ND	ND a
Coronene	ND	.0004 (ND-.001) ab
Dibenzo(ah)anthracene	ND	.0007 (ND-.002) ab
7H-Dibenzo(cg)carbazole		ND b
Fluorene	ND	ND a
Fluoranthene	ND	.42 (ND-.66) ab
Indeno(1,2,3-cd)pyrene		.0001 a
Methylphenanthrenes	ND	ND a
Perylene	ND	.001 (ND-.002) ab
Phenanthrene	ND	ND a
Pyrene	ND	.51 (ND-.78) ab
Triphenylene	ND	ND a
Total PAH		2.67 a

Notes

a Shih et al 1980. Factors represent total of particulate and gaseous PAH. Natural gas-fired sites tested: 3 tangentially fired, 90 to 193 MW operating capacity, 79 to 107% of base load; 5 wall fired units, 19.5 to 162 MW operating capacity, 65 to 95% of base load. Residual oil-fired sites tested: 4 tangentially fired, 42 to 548 MW operating capacity, 86 to 105% of base load; 10 tests at 7 wall fired sites, 43 to 702 MW operating capacity, 81 to 108% of base load.

b Zelinski et al 1980. Factors represent total of gaseous and particulate PAH. No specifics provided on boiler. U.S. EPA (1987a) reports no controls on the 5 units tested.

TABLE 5.1.4

Average PCB, PCDD and PCDF Emission Factors (and Ranges) for Utility Boilers

	Bituminous Coal[ac] (All Boilers)	Lignite,[ad] Anthracite Coal	Natural[bd] Gas	Distillate[bd] Oil	Residual[bd] Oil
PCBs					
T_3CB	ND				
T_4CB	.057 (ND-.114)				
P_5CB	.520 (ND-.114)				
H_6CB	.044 (ND-.088)				
H_7CB	.027 (ND-.052)				
O_8CB	ND				
N_9CB	ND				
DCB	ND				
Total PCB					
PCDDs					
T_4CDD	.0108 (.0079-.0137)				
P_5CDD	.0035 (ND-.0070)				
H_6CDD	.0019 (ND-.0038)				
H_7CDD	.0015 (ND-.0029)				
O_8CDD	ND				
2,3,7,8-T_4CDD					
Total PCDD		ND	ND	ND	ND
PCDFs					
T_4CDF	.0279 (.0273-.0284)				
P_5CDF	.0234 (.0173-.0295)				
H_6CDF	.0077 (ND-.0153)				
H_7CDF	.0012 (ND-.0023)				
O_8CDF	ND				
2,3,7,8-T_4CDF					
Total PCDF		ND	ND	ND	ND

a mg/tonne
b mg/KL
c Based on one test series by Thorndyke (1988). Four pulverized dry bottom units, ESP controlled, were tested. This data was chosen in preference to data reported in TIER 4 (U.S. EPA 1987e) because of lower reported detection limits.
d Based on a literature review conducted as part of the National Dioxin Study Tier 4 (U.S. EPA 1987e)

5.2 Industrial Fuel Combustion

5.2.1 Source Description

Stationary external combustion sources are primarily used in industry for the generation of process steam and space heating. Some units are also used for electricity generation. The use of internal combustion units in industry is discussed in Section 5.7. Fuels used in industrial external combustion systems include bituminous, anthracite and lignite coal, wood, residual oil, distillate oil and natural gas. The use of wood as a fuel for industrial combustors is discussed in Section 5.3.

Table 5.2.1 shows the major combustion systems in this sector for the U.S. in 1985. Bituminous dry-pulverized and spreader stoker coal-fired units are the most common large-sized coal-fired unit, while smaller needs are more commonly met with underfeed and overfeed stokers. Lignite and anthracite coal are usually burned in stokers. Oil and natural gas burning units are usually watertube or firetube boilers. In firetube boilers, the combustion gases pass through tubes submerged in water. In a watertube system the combustion gases transfer heat to tubes in which water is fed to be converted to steam. Further details on all of these systems are provided in the section on electric utility boilers, Section 5.1. (Surprenant et al 1981b, U.S. EPA 1987a)

Emissions control on industrial boilers is mainly directed at reducing particulate flue gas emissions from coal-fired boilers. This is achieved by using baghouses, ESPs, wet scrubbers and multicyclones. Flue gas desulphurization (FGD) units for SO_2 control are much less common in industrial coal-fired units than in the utility sector, but are used. SO_2 control is more commonly achieved through the use of low sulphur coal. (Surprenant et al 1981b, U.S. EPA 1987a)

Particulate emissions from oil-fired industrial combustors are usually not controlled. Any units with potential excessive SO_2 emissions usually switch to low sulfur oils rather than install emission controls. Natural gas units also do not usually have any sort of emissions control. (U.S. EPA 1987a)

5.2.2 Emission Factors

PAH emission factors for industrial stationary fuel combustion are presented in Table 5.2.2. Specifics on the tests used to derive these emission factors are provided in detailed notes to these tables. As for all tests reported by Hangebrauk et al 1967, there is some question as to whether the results are for particulate PAH or for total (particulate plus gaseous) PAH.

No PAH emission data was found for anthracite or lignite-fueled industrial boilers.

Very limited data was found for PCB, PCDD and PCDF emissions from industrial combustion sources. Table 5.2.3 summarizes the results of limited tests on a bituminous coal-fired coal dryer. This test was considered not to be representative of all industrial coal combustors, as emission rates of various compounds were high. Therefore, PCB, PCDD and PCDF emission rates presented in Table 5.2.3 were averaged with those for utility coal combustors to estimate emission rates for a typical industrial bituminous coal-fired boiler.

5.2.3 Inventory Comments

The emission factor data discussed in the previous section was used to derive emission factor files as follows:

Fuel Master Sector Code, Fuel	Emission Factor Files	Units
anthracite 20201	PAH - bituminous stoker - bituminous pulverized (assigned to cyclone as well) PCDD, PCDF, PCB - bituminous - all boilers	mg/tonne
bituminous, sub bituminous 20203	PAH - bituminous stoker - bituminouspulverized (assigned to cyclone as well) PCDD, PCDF, PCB - bituminous-all boilers	mg/tonne
lignite 20203	PAH - lignite, all boilers from electric utility	mg/tonne
residual oil 20204	PAH - all boilers	mg/kL
distillate oil 20205	PAH - all boilers	mg/tonne
natural gas 20206	PAH - all boilers	mg/tonne

Point sources (P) from MOE (O) or NAPAP (N) (where base quantities were non-zero) and area sources (A) from MOE or NAPAP (base quantities back-calculated from area source emission rates using AP-42 emission factors) were inventoried as follows:

Master Sector Code	Ontario	Can. (other)	U.S.
20201	-	-	NA,NP
20202	OA,OP	NA	NA,NP
20203	-	-	NP
20204	OA,OP	NA,NP	NA,NP
20205	OA,OP	NA	NA,NP
20206	OA,OP	NA,NP	NA,NP

The NAPAP point sources included those from fuel-fired equipment and in-process fuel as well as the industrial combustion SCC's. Temporal factors are point specific.

For area sources, Ontario and U.S. emissions were already gridded. Canada (other) area sources , available as provincial totals, were gridded using industrial labour force as a spatial allocation surrogate. Temporal factors for Ontario and Canada (other) emissions were from the U.S. Michigan area source temporal factor file for the appropriate industrial fuel use.

TABLE 5.2.1

Classification of External Combustion Systems for Industrial Applications With Predicted U.S. Fuel Consumption for 1985 (Surprenant et al 1981b)

	Predicted 1985 Fuel Consumption (10^{15} joules)	% of Total Fuel Consumption
External Combustion	10320	100
Coal	2002	19.4
Bituminous	1955	18.9
Pulverized, dry	876	8.5
Pulverized, wet	81	.8
Cyclone	14	.1
Spreader Stokers	916	8.9
Other Stokers	68	.7
Anthracite	7	<.1
All Stokers	7	<.1
Lignite	40	3.9
Spreader Stokers	40	3.9
Petroleum	2308	22.4
Residual Oil	2028	19.7
Distillate Oil	280	2.7
Gas	5470	53.0
Other	540	5.2

TABLE 5.2.2

Average PAH Emission Factors (and Ranges) for Industrial Fuel Combustion

	Bituminous Coal (mg/tonne)		Natural Gas	Residual Oil	Distillate Oil
	Pulverized (Wet & Dry)	Stoker	(mg/kL)	(mg/kL)	(mg/kL)
Acenaphthene		97.1 d			
Acenaphthylene		18.4 d			
Anthracene	1.8 (ND-11) ab	24.2 (ND-470) abde	ND ab	ND ab	ND ab
Benz(a)anthracene	ND a	.42 (ND-6.1) ae	ND a	ND a	ND a
Benzo(b)fluoranthene	ND a	ND a	ND a	ND a	ND a
Benzo(k)fluoranthene	ND a	ND a	ND a	ND a	
Benzofluoranthenes	310 c	.73 (.22-2.5) e			
Benzo(a)fluorene	ND a	.95 (ND-3.8) ad	ND a	ND a	ND a
Benzo(ghi)perylene	.04 (ND-.224) a	11 (ND-140) abde	ND a	ND a	
Benzo(a)pyrene	0.14 ·ND-.95) abc	23 (.17-310) bde	.1 (ND-1) ab	.32 (ND-1.9) ab	.1 (ND-.6) ab
Benzo(e)pyrene	0.39 (ND-2.7) abc	19 (.17-240) bde	ND ab	ND ab	ND ab
Carbazole			.001 (ND-.013) a		
Chrysene	ND a	1.1 (.22-2.3) e	ND a	ND a	ND a
Coronene	ND abc	1.1 (ND-10) abe	ND a	ND ab	ND ab
Dibenz(ah)anthracene	12 c	ND ad	ND a		
7H-Dibenzo(cg)carbazole	ND c				
Fluoranthene	24 (ND-150) abc	126 (ND-1200) abde	.29 (ND-3.0) ab	1.7 (ND-10) ab	.32 (ND-1.6) ab
Fluorene	ND a	20 (ND-80) ad	ND a	ND a	ND a
Indeno(1,2,3-cd)pyrene	2.8 c	.62 (ND-2.5) ade			
Methylanthracenes	ND a	ND a	ND a	ND a	ND a
Methylphenanthrenes	ND a	ND a	ND a	ND a	ND b
Perylene	ND abc	3.1 (ND-49) abde	ND ab	ND ab	ND ab
Phenanthrene	8.4 (ND-50.4) abc	154 (ND-1525) abde	.002 (ND-.003) ab	12 (ND-71) ab	ND a
Pyrene	1.9 (ND-6.2) abc	118 (ND-1450) abde	.43 (ND-4.7) ab	2.0 (ND-12) ab	.3 (ND-1.4) ab
Triphenylene	ND a	ND a	ND a	ND a	ND a

TABLE 5.2.2 (contd.)

Average PAH Emission Factors (and Ranges) for Industrial Fuel Combustion

Notes

a Surprenant et al 1981b. Factors represent total of particulate and gaseous PAH. Bituminous pulverized tests: 5 sites were tested (3 wet, 2 dry); 34-75 MW rated capacity; 61-89% of base load; 4 with multicyclone, 2 with ESP, 1 with FGD unit. Bituminous stoker tests: 3 sites, all spreader; 131-158 MW rated capacity; 40-91% of base load; all with multicyclone, 1 with additional ESP. Gas-fired tests: 10 sites, 2 firetube, 1 scotch, 7 watertube; 8-178 MW rated capacity; 30-80% of base load; no pollution control. Residual oil sites: 5 sites, 4 field-watertube, 1 drumless serpentine; 42-117 MW rated capacity; 60-93% of base load; 1 with multicyclone and FGD unit, remainder no pollution control. Distilllate oil sites: 4 sites, all field watertube; 42-155 MW rated capacity; 39-93% of base load; no pollution control devices.

b Hangebrauk et al 1967. It is unclear whether emission factor represents total of particulate and gaseous emissions (see text). Bituminous pulverized: 1 dry bottom watertube unit tested, 200,000 lb steam capacity with multicyclone, tested at 53% base load. Bituminous stoker, 2 units tested: one watertube boiler, spreader stoker, 70,500 lb steam capacity, 70% of base load during test, multiple cyclone; one firetube boiler, underfeed stoker, 3.8×10^6 BTU rated capacity, 79% of base load, no emissions control. Natural gas-fired unit tested was a firetube boiler with a premix burner, 7.2×10^6 BTU rated capacity, 129% of base load, no pollution control. Residual oil-fired unit is a watertube boiler, steam atomized, 30×10^6 BTU rated capacity, tested at 48% base load, no controls. The distillate oil-fired unit tested was also a steam-atomized watertube boiler, 23×10^6 BTU operating capacity, tested at 91% of baseload, no controls.

c McCarley et al 1979, as cited by Surprenant et al, 1981. 1 unit was reported as tested: bituminous pulverized coal-fired, watertube boiler with 132 GJ/hr fuel capacity; operating load not known; ESP controlled.

d Burlingame et al 1981. Factor represents total of gaseous and particulate PAH. 11 coal fired stoker units were tested: 6 spreader, steam capacity 75,000 to 300,000 (lbs assumed), 66-99% of base load, 3 ESP and 3 "dust collector" controlled; 5 overfeed, 45,000 to 90,000 (lbs assumed) steam capacity, 59 to 102% of base load, 2 no control and 3 with a "dust collector".

e Environment Canada 1985. Factor represents total of particulate and gaseous emissions. Bituminous coal-fired stoker, 3 tonnes/h burn rate, cyclone and venturi scrubber controlled.

TABLE 5.2.3

PCB, PCDD and PCDF Emission Factors for a Bituminous Coal-Fired Stoker[a]

	Emission Rate (mg/tonne)
Total PCDD	0.169
T_4 CDF	0.023
Total PCB	3-26

(a) Environment Canada 1985. Factor represents total of gaseous and particulate emissions. Stoker had a 3 tonnes/hr burn rate, cyclones and venturi scrubber controlled.

5.3 Industrial Wood Combustion

5.3.1 Source Description

The use of wood-fired industrial boilers is largely confined to industries where wood waste is available as a byproduct. Wood waste may include large pieces like slabs, log and bark strips, as well as cuttings, shavings, pellets and sawdust. Generally bark is a major type of waste burned at pulp mills and a varying mixture of wood alone or wood and bark waste is burned in the lumber, furniture and plywood industries (U.S. EPA 1985). Other sectors that use wood waste as a boiler fuel vary widely, ranging from other industries to utilities and institutions. The decision to use wood waste as a fuel seems to depend more on the availability of a nearby dependable supply source than on the type of industry (Young and Ostermeir 1987).

Many boiler configurations are used in burning wood waste. The dutch oven is very common since it burns fuels with high moisture. It takes place in two stages: drying and gasification, and combustion of gaseous products. This oven is not responsive to load changes and provides poor combustion control (U.S. EPA 1985).

In the fuel cell oven, fuel is dropped into suspended fixed grates and is fired in a pile. The fuel cell oven uses combustion air preheating and repositioning of air injection ports to improve boiler efficiency over that of the dutch oven (U.S. EPA 1985).

Modified conventional boilers are also used in many large operations. These modified units include spreader stokers, tangentially- fired or cyclone-fired boilers. The spreader stoker is most common, has a fast response to load changes, has improved combustion control and can be operated with multiple fuels (U.S. EPA 1985).

Major factors affecting emissions from wood waste boilers include: the composition of the waste fuel burned; the degree of flyash reinjection employed, and furnace design and operating conditons (U.S. EPA 1985). Emissions from these boilers are typically controlled by multicyclones followed by venturi or impingement-type wet scrubbers. ESPs are also used, although much less commonly. It is estimated that there is potentially good particulate and vaporous PAH control with scrubbers and effective particulate but no vaporous PAH control with ESPs (U.S. EPA 1987a).

5.3.2 Emission Factors

The PAH emission factors listed in Table 5.3.1 are averaged from tests reported in Alsberg and Stenberg (1979), Surprenant et al (1981b) and Wainwright et al (1982). All tests represent the total of particulate and gaseous PAH emissions. The sources tested represent a wide range of situations: boiler types vary widely, including horizontal return tube boilers, underfeed stoker, fluidized bed and dutch ovens; varying wood feed systems ranging from chute feed with a pneumatic spreader to manual feeding; various fuel types including wood chips, bark, sawdust and hardwood, ranging from green to kiln-dried; and varying emissions control, including no control, multicyclones and scrubbers.

No PCB emission factors were identified for industrial wood combustion. PCDD and PCDF emissions from an industrial boiler burning primarily wet salt-laden wood was tested as part of the Tier 4 program (U.S. EPA 19897e). These results, presented in Table 5.3.2, are considered to represent a maximum emission rate for controlled industrial wood boilers. No other PCDD/PCDF emission factors were identified for this sector.

5.3.3 Inventory Comments

The average emission factors for PAH, PCDD and PCDF discussed in Section 5.3.2 were applied to industrial wood combustion point (P) and area (A) sources using data from NAPAP files (N) and the Ontario Ministry of Environment (O) as follows:

Master Sector Code	Ontario	Can. (other)	U.S.
20602	OA,OP	-	NP,NA

Only those NAPAP point sources with non zero base quantities were inventoried. Temporal factors are point specific.

Area source base quantities for the U.S. were back-calculated using AP-42 emission factors. All data was gridded. Temporal factors for Ontario were taken from the Michigan area source temporal file for industrial wood combustion.

TABLE 5.3.1

PAH Emission Factors for Industrial Wood Combustion (mg/tonne wood)

	Average**	n***	Range
Anthracene	52	28	ND-290
Benzo(a)fluorene	0	5	
Benzo(a)pyrene	59	28	ND-290
Benzo(e)pyrene	13	23	ND-64
Benzo(b)fluoranthene	82	28	ND-380
Benzo(k)fluoranthene	3.0	28	ND-13
Benz(a)anthracene	24	28	ND-260
Benzo(ghi)perylene	5.8	28	ND-60
Coronene	0	8	
Chrysene	46	25	ND-220
Cyclopenta(cd)pyrene	14	3	4-25
Dibenz(ah)anthracene	1.8	20	ND-36
Fluorene	43	25	ND-270
Fluoranthene	188	28	ND-810
Indeno(1,2,3-cd)pyrene	3.3	23	ND-26
Methylanthracenes	0	5	
Methylphenanthrenes*	6.0	20	ND-38
Perylene	0.4	28	ND-5.3
Pyrene	155	28	ND-590
Phenanthrene	990	28	ND-4600

Notes:

* Represents total of 1- and 9-methylphenanthrene

** ND was always taken as 0 in computing averages. References used were Surprenant et al, 1981 Wainwright et al 1982 and Alsberg and Stenberg 1979.

*** n is the number of tests used to compute the average.

TABLE 5.3.2

PCDD and PCDF Emission Factors for Industrial Wood Combustors* (mg/tonne wood feed)

Isomer	Average	Range
Dioxins		
2,3,7,8 TCDD	.000987	.000760-.00112
Other T_4CDD	.174	.0905-.255
P_5CDD	.177	.0726-.233
H_6CDD	.181	.0744-.238
H_7CDD	.139	.113-.180
O_8CDD	.0398	.0357-.0454
Total PCDD	.711	.390-.952
Furans		
2,3,7,8 TCDF	.00629	.00494-.00721
Other T_4CDF	.137	.0800-.207
P_5CDF	.0852	.0477-.122
H_6CDF	.0496	.131-.0818
H_7CDF	.0241	.0119-.0377
O_8CDF	.00329	.00224-.00456
Total PCDF	.306	.162-.459

* U.S. EPA 1987e. A dutch oven boiler with 5900 kg/hr dry wood semi-continuous feed was tested three times. This unit was baghouse controlled. See text for further details.

5.4 Commercial/Institutional Fuel Combustion

5.4.1 Source Description

This category includes external combustion sources used for space/water heating in commercial establishments, health and educational institutions and government/public administration facilities. Internal combustion sources used by this sector (primarily gas and oil-fired reciprocating engines used for pumping water and sewage) are discussed in section 5.7.

Commercial/institutional external combustion sources may be classifed by the boiler/furnace design or type of fuel. Further characterizations include installed capacity and firing method. Table 5.4.1 lists the major types of units along with their principle fuel types and capacity ranges. In the United States most of the smaller units (<13.2 J/hr) are cast iron or firetube units. Watertube units constitute 100 percent of all units above 50×10^9 J/hr. (Surprenant et al 1981a)

Table 5.4.2. summarizes recent Canadian and U.S. commercial/ institutional fuel consumption, expressed as a percent of total joules consumed. Natural gas and petroleum products represent almost 100% of the energy consumption in this sector for both countries.

Air pollution control equipment is usually not installed on commercial/ institutional combustion units. Some of the larger units, particularly the coal-fired boilers (pulverized or stoker), do have controls. These have automated particulate control efficiencies of 40% for pulverized units (primarily dry bottom) and 20% for all stokers, based on data in the U.S. NEDS system. Gas and oil-fired units are usually uncontrolled, although proper equipment selection, maintenance and operating practices can be used to limit emissions. (Surprenant et al 1981a)

5.4.2 Emission Factors

Emission factors for industrial/commercial external combustion sources are summarized in Table 5.4.3. Details of the sources tested are provided in Table 5.4.4. This summary is based on an emissions assessment of these sources (Surprenant et al 1981a), which involved a critical evaluation of (then) existing emissions data, followed by a measurement program designed to fill data gaps based on a phased sampling and analysis strategy. Although Hangebrauk (1967) measured emissions of some PAHs for commercial/institutional boilers, the data measured by Surprenant et al (1981a) was felt to be more representative of current emissions and so was used exclusively in PAH emission factor derivation for this sector.

Details of the field and laboratory methods can be found in Surprenant et al 1981a.

In general, the study concluded that, with the exception of wood-fired and bituminous coal-fired stoker units, commercial/industrial external combustion units did not have significant POM emissions. Napthalene, at low levels, was identified as the principal POM emitted. One gas-fired boiler did emit compounds such as phenanthrene, fluoranthene and pyrene (see Table 5.4.3). It was felt that low excess air operation (~10 percent) accounted for the relatively high emissions from this site. (Surprenant et al 1981a)

The underfeed stoker unit tested during this program was found to emit significant levels of POM when it was fired with bituminous coal or wood. This unit was run at low heat input levels for both tests. It was felt that this resulted in lower than normal combustion levels and possibly inefficient combustion, factors that appear to favour PAH formation. It was also noted that more detailed analytical procedures would be required to confirm the emission estimates from this study. (Surprenant et al 1981a)

No PCB, PCDD or PCDF emission factors were identified for commercial/institutional fuel combustion.

5.4.3 Inventory Comments

Bituminous coal-fired stokers were inventoried using the no control PAH emission factors listed in Table 5.4.3. Average PAH emission factors for commercial/institutional combustors were used for the remaining fuels (bituminous (non stoker), anthracite, lignite, residual oil, distillate oil and natural gas and wood. PCDD, PCDF and PCB were not inventoried for these sources, with the exception of wood, for which industrial wood combustion factors were used.

Commercial/institutional external combustion sources are inventoried as both point (P) and area (A) sources, using data from the Ontario Ministry of the Environment (O) and NAPAP (N) as follows:

Fuel/Master Sector Code	Ontario	Can. (other)	U.S.
Anthracite-20302	-	-	NA,NP
Bituminous,Subbituminous 20302	OP	NA	NA,NP
Lignite-20303	-	-	NA,NP
Residual Oil-20304	OA,OP	NA	NA,NP
Distillate Oil-20305	OA,OP	NA	NA,NP
Natural Gas-20306	OA,OP	NA	NA,NP
Wood-20603	-	-	NP

For point sources, only those with non-zero base quantities were inventoried. Space heaters for commercial/institutional uses were included. Temporal codes are point specific.

For area sources other than in Ontario, base quantities were obtained from NAPAP emissons files by back calculating using AP-42 (U.S. EPA 1985) emission factors. Temporal factors for Ontario and Canada (other) were taken from the appropriate Michigan area SCC temporal factor file. Ontario and U.S. area data were already gridded. Canada (other) data was available on a provincial basis and was gridded using commercial labour force as a spatial allocation factor.

TABLE 5.4.1

Commercial/Institutional External Combustion Sources

Unit Type	Principle Fuel Type	Rated Capacity
Warm air Furnaces	natural gas or oil	small
Cast Iron Boiler Systems	natural gas and distillate oil	up to 13.2 x 10^9 J/hr
Firetube Boilers	natural gas and oil (larger units - residual and distillate, smaller units - distillate)	from 5 to 26 x 10^9 J/hr
Watertube Boilers	natural gas, oil or coal	almost exclusively over 50 x 10^9 J/hr

Extracted from Surprenant et al 1981a.

TABLE 5.4.2

Canadian and United States Commercial/Institutional Fuel Consumption (Expressed as Percent of Total Joules Consumed in the Year Indicated)

Fuel Type	Canadian[1] Consumption (1980)	U.S. Predicted[2] Consumption (1985)
Coal	-	3
Residual Oil	<1	25
Distillate Oil	17	21
Natural Gas	82	48
Kerosene	1	-
Bottled Gas	<1	-
Wood	-	2

1. Based on Ontario Research Foundation 1983.

2. Extracted from Surprenant et al 1981a.

TABLE 5.4.3

Commercial/Institutional External Combustion Emission Factors[1]

	Coal (mg/tonne)			Natural Gas (mg/kL)	Residual Oil (mg/kL)	Distillate Oil (mg/kL)	Wood (mg/tonne)
	Bit Stoker		All Other				
	Controlled	No Control					
Anthracene	ND	ND	ND	ND	ND	ND	ND
Acenaphthylene				.08 (ND-.326)			
Benzo(a)fluorene	ND	ND	ND	ND	ND	ND	ND
Benzo(a)pyrene	ND	4984	ND	ND	ND	ND	60554
Benzo(e)pyrene	ND	ND	ND	ND	ND	ND	ND
Benzo(b)fluoranthene	ND	ND	ND	ND	ND	ND	ND
Benzo(k)fluoranthene	ND	ND	ND	ND	ND	ND	ND
Benz(a)anthracene	ND	3696	ND	ND	ND	ND	ND
Benzo(ghi)perylene	ND	1344	ND	ND	ND	ND	40970
Chrysene	ND	616	ND	ND	ND	ND	8908
Coronene	ND	ND	ND	ND	ND	ND	ND
Dibenz(ah)anthracene	ND	700	ND	ND	ND	ND	6681
Fluorene	ND	ND	ND	ND	ND	ND	15810
Fluoranthene	ND	6916	ND	.007 (ND-.034)	ND	ND	11084
Methylanthracenes	ND	ND	ND	ND	ND	ND	ND
Methylphenanthrenes	ND	1064	ND	ND	ND	ND	17544
Perylene	ND	ND	ND	ND	ND	ND	ND
Phenanthrene	ND	8092	ND	.01 (0-.054)	ND	ND	75769
Pyrene	ND	6972	ND	.03 (0-.131)	ND	ND	38437
Triphenylene	ND	ND	ND	ND	ND	ND	ND

1. All emission factors are based on Suprenant et al 1981a.

TABLE 5.4.4

Characteristics of Commercial/Institutional External Combustion Sources Tested for Emission Factors in Table 5.4.3

Fuel Type	Boiler Type	No. of Units Tested	Range of Capabilities (GJ/hr)	Range of Based Load Tested (%)	Pollution Control
Coal - bituminous stokers	NA	3	2.3-26	41-100	ESPs and no control
- all other (bituminous pulverized, anthracite stokers)	NA	5	9.2-148	79-100	1 multicyclone, others no control
Natural Gas	all watertube	5	18-132	66-85	no control
Residual Oil	4 watertube, 1 firetube	5	1.8-132	66-85	no control
Distillate Oil	2 watertube, 1 cast iron	3	5.3-37	80	no control
Wood	underfeed stoker	1	2.3	41	no control

Extracted from Suprenant et al 1981a.

5.5 Residential Fuel Combustion

5.5.1 Source Description

This sector includes the use of natural gas, distillate oil and bituminous and anthracite coal for residential space and hot water heating purposes. Residential wood combustion is discussed in Section 5.6. Residual oil has little use in domestic applications, as it must be heated to facilitate handling and proper atomization. (U.S. EPA 1985)

Distillate oil and gas-fired residential furnaces have numerous burner configurations, designed to try to optimize the efficiency of fuel combustion. In natural gas-fired units the fuel is usually premixed with excess air (commonly 10 to 15 percent) prior to injection in the burner to increase combustion efficiency. Distillate oil-fired units may use pressure or vaporization to atomize fuel oil. This produces finer droplets for combustion, which usually increases combustion efficiency and decreases the formation of polycyclic organic compounds. (U.S. EPA 1985, U.S. EPA 1987a)

Residential coal-fired furnaces are usually underfeed or hand-stoked units. Boilers, used for steam or hot water production, and warm-air fumaces are usually stoker fed and automatically controlled by a thermostat. These are usually designed for a specific type of coal. Other hand-fed residential coal combusters, usually used for auxiliary heating, include room heaters, metal stoves and metal and masonary fireplaces. The majority of the coal burned for this purpose is butuminous or anthracite coal; lignite coal is an insignificant portion of the total. (U.S. EPA 1987a, DeAngelis and Reznik 1979)

Residential combustion units do not usually have particulate or gaseous pollutant control devices. However, proper design, use and maintenance of each unit can decrease the emissions. These involve such changes in fuel

properties (i.e., cleaning coal), fuel type, firing rate, firing equipment design, modified combustion air flow control, better thermal control and heat storage and the cyclic operation of automatic equipment. (U.S. EPA 1987a, De Angelis and Reznik 1979)

5.5.2 Emission Factors

Table 5.5.1 summarizes average PAH emission factors and ranges for residential fuel combustion sources.

The natural gas emission factors are based on Hangebrauck et al 1967. The technique used in this study is under some dispute. U.S. EPA (1987a) states in some sections that these tests represent primarily particulate; other sections indicate that they represent the sum of gaseous and particulate emissions for the PAHs tested. Three tests were conducted on units with pre-mix burners. One of the three tests conducted produced significantly higher levels of PAHs. It was thought that this was due to improper adjustment of the air-fuel ratio as evidenced by high concentrations of CO and total gaseous hydrocarbons.

The emissions factors for distillate oil-fueled units are based on Hangebrauk et al 1967 and Smith 1984. Hangebrauk (see comment above) tested two pressure atomized and one vaporized units, with no significant differences in emissions for the units. In the literature review by Smith 1984 the total (vapour and particulate phase) emissions were reported for one of each type of unit. The vaporising pot burner was found to have significantly higher emissions than the high pressure jet burner for all PAHs analysed.

Coal-fired residential units were investigated by Sanborn et al 1985, Giammar et al 1976 and DeAngelis and Reznik 1979. A wide variety of units were investigated, including boilers, furnaces, coal-burning stoves and wood-burning stoves burning coal. Hand-fed and automatically-fed units

were compared. Emissions from the "on" portion of heating cycles vs. "off"-portions were also investigated. A number of conclusions were made:

- coals that had the high volatile matter content and the highest free-swelling index had the highest levels of POM emissions (Giammar et al 1976, DeAngelis and Reznik 1979).

- anthracite generated the lowest POM emissions (Giammar et al 1976, Sanborn et al 1985).

- POM formation during combustion depends strongly on combustion efficiency which varies widely from unit to unit. In spite of high excess air levels in these units, non-uniform beds and other aspects of the unit favour the formation of POMs. High excess air levels may actually favour POM formation by faster quenching in the post-flame region and by reducing retention times in the combustion chamber. This inverse relationship between POM formation and combustion efficiency accounts for higher POM emission rates from hand-fed units and the OFF portion of a heating cycle. (DeAngelis and Reznik 1979.)

DeAngelis and Reznik, 1979, also reported that PCBs were not found in the emissions from a residential bituminous coal-fired unit. Detection limits were 5 µg/kg of coal. Anthracite and lignite-fired units were not tested.

PCDD and PCDF measurements were only identified for chimney soot from coal and oil-fired residential combustion units. Average PCDD and PCDF concentrations in chimney soot (see Table 5.5.2) were applied to typical particulate emission rates for these units (U.S. EPA 1985) in order to derive the particulate dioxin and furan emission factors presented in Table 5.5.3. No details are available on the units tested. It must be emphasized that these emission factors represent the maximum emission rates from these units, as

chimney soot is not necessarily representative of the particulate actually emitted to the atmosphere.

The literature review conducted as part of the Tier 4 study (U.S. EPA 1987e) reviewed a study by Dow, in which particulate matter removed from a home electrostatic precipitator in a residential, natural gas-fired forced-air heating system was analysed for selected dioxins. This data was not used here as it was not considered to be representative of emissions from residential natural gas-fired furnaces to the atmosphere.

5.5.3 Inventory Comments

Emission factors from Tables 5.5.1 (PAH), and 5.5.2 (PCDD and PCDF) were used as follows:

Master Sector Code, Fuel			Emission Factor Files	Units
coal 20401	bituminous	-	PAH-bituminous	mg/tonne
		-	PCDD, PCDF coal	
	anthracite	-	PAH anthracite	
		-	PCDD, PCDF coal	
residual oil 20402	PAH	-	distillate oil	mg/kL
	PCDD, PCDF	-	oil central heating	
distillate oil 20403	PAH	-	distillate oil	mg/kL
	PCDD, PCDF	-	oil central heating	
natural gas 20404	PAH	-	natural gas (no PCDD, PCDF)	mg/KL

All residential fuel combustion sources were inventoried as area sources.

Ontario base quantity data was supplied by the Ontario Ministry of the Environment. Residential and multiple dwelling fuel use was included under each grouping. No coal was used residentially in Ontario. Data was available on the UTM grid.

Canada (other) base quantities were derived using NAPAP (AP-42) (U.S. EPA 1985) TSP emission factors and total TSP emissions. The emissions were spatially allocated using the following surrogates:

- coal - total dwellings
- residual oil - oil dwellings
- distillate oil - oil dwellings
- natural gas - gas dwellings

For the U.S., fuel use was derived from TSP emissions and emission factors from NAPAP by county. Spatial allaocation was completed using the county centroid file.

Temporal factors were available for each sector for each state in the U.S. The appropriate temporal code for Michigan was used for Ontario and Canada (other) residential combustion.

TABLE 5.5.1

PAH Emission Factor Summary for Residential Fuel Combustion (Wood Excluded)

Compound	Bituminous Coal (mg/tonne)	Anthracite Coal (mg/tonne)	Natural Gas[d] (mg/kL)	Distillate Oil (mg/kL)
Acenapthene	17000 (760-39000) ac	13 (6-21) a		
Acenapthylene	12000 (640-26000) a	59 (6-160) a		
Anthracene	3100 (400-4900) a	14 (4-23) a	ND	ND d
Benz(a)anthracene	3000 (1800-4250) a	35 (6-68) a		65 (.05-130) e
Benzofluoranthene	5900 (400-16000) b	100 (44-160) b		
Benzo(ghi)perylene	830 (24-3300) ab	2.0 (.79-3.9) ab	.025 (ND-.074)	6 (ND-30) de
Benzo(a)pyrene	2600 (2100-3000) a	3.2 (1.3-4.3) a	.004 (ND-.011)	2.3 (ND-12) de
Benzo(e)pyrene	2000 (1500-2300) a	3.8 (2.0-7.5) a	.017 (ND-.050)	15 (ND-74) de
Chrysene	2800 (1500-3500) a	32 (10-74) a		
Coronene			.009 (ND-.028)	4.3 (ND-17) de
Dibenz(ah)anthracene	670 (ND-3000) bc	ND b		
7H-Dibenzo(cg)carbazole	ND bc	ND b		
Fluorene	13000 (3600-26000) ac	15 (4-30) a		
Fluoranthene	7700 (770-35000) abc	71 (16-120) ab	.096 (.005-.270)	470 (1-2090) de
Indeno(1,2,3-cd)pyrene	1100 (31-2900) abc	2.9 (1.3-4.6) ab		
Methylanthracenes	8200 (1100-29000) b	100 (46-160) b		
Methylphenanthrenes	1800 bc			
Perylene	530 (ND-4000) ab	.45 (ND-1.0) ab	ND	.9 (ND-3.6) de
Phenanthrene	11000 (7200-18000) a	137 (41-230) a	.001 (ND-.003)	120 (ND-370) d
Pyrene	6000 (460-24000) abc	66 (13-120) ab	.180 (.005-.540)	170 (.3-722) de
Total PAH	71000 (12000-190000) b	1100 (260-1900) b		

TABLE 5.5.1 (contd.)

PAH Emission Factor Summary for Residential Fuel Combustion (Wood Excluded)

Notes

a Sanborn et al 1985. Results are for 3 emissions tests, for both bituminous and anthracite on: a coal stove, low and high burn rate; a wood stove burning coal, moderate burn rate. Factors represent total of particulate and vapour PAH.

b Giammar et al 1976. Seven bituminous coal-fired and two anthracite coal-fired tests on a 200 kw boiler. No controls used. Results are total of particulate and vapour PAH.

c DeAngelis and Reznik 1979. Average of one test on a coal-fired boiler and one test on a coal-fired furnace (both bituminous). Factors represent total of particulate and vapour PAH.

d Hangebrauck et al 1967. See text for details.

e Smith 1984. Literature review.

TABLE 5.5.2

Average and Ranges of PCDD and PCDF in Chimney Soot from Coal and Oil-Fired Residential Combustors (μg/kg of soot)*

Compound	Coal Oven (n=7)	Oil Central Heating (n-21)
Dioxins		
TCDD-2,3,7,8	.3196 (.1182-.7497)	.0186 (ND - .0685)
T_4CDD	11.950 (2.460 - 44.986)	.2761 (.0064 - 1.950)
P_5CDD	6.192 (.8400-17.370)	.2741 (.0050 - 3.600)
H_6CDD	11.953 (1.550 - 33.093)	.2202 (.0104 - 2.400)
H_7CDD	11.447 (1.200 - 39.242)	.2095 (.0190 - 1.100)
O_8CDD	15.416 (.950 - 56.355)	.2191 (.0338 - .5642)
Furans		
TCDF-2,3,7,8	8.408 (.5979 - 25.142)	.1754 (.0039 - 1.500)
T_4CDF	73.322 (8.040 - 256.070)	2.0409 (.0317 - 24.500)
P_5CDF	67.809 (6.510 - 196.963)	1.3951 (.0403 - 16.900)
H_6CDF	25.494 (2.290-68.030)	.5755 (.0280 - 8.100)
H_7CDF	6.329 (.6921 - 9.952)	.2420 (.0104 - 3.800)
O_8CDF	.839 (.1555 - 1.800)	.0988 (.0074 - 1.500)

* Thoma 1988. Chimney soot samples were collected from 7 coal ovens and 21 furnaces (central heating) in the area of Bayreuth, Germany.

TABLE 5.5.3

PCDD and PCDF Emission Factors for Coal and Oil-Fired Residential Combustors*

Compound	Coal Oven (mg/tonne coal burned) Anthracite	Bituminous	Oil Central Heating (mg/kL)
Dioxins			
TCDD-2,3,7,8	.0016	.0024	.0000056
T_4CDD	.060	.090	.000083
P_5CDD	.031	.046	.000082
H_6CDD	.060	.090	.000066
H_7CDD	.057	.086	.000063
O_8CDD	.077	.120	.000066
Furans			
TCDF-2,3,7,8	.042	.063	.000053
T_4CDF	.370	.550	.00061
P_5CDF	.340	.510	.00042
H_6CDF	.130	.190	.00017
H_7CDF	.032	.047	.000073
O_8CDF	.0042	.0063	.000030

* Based on average emission factors presented in Table 5.5.2 and particulate emission rates from AP-42 (U.S. EPA 1985) as follows:

coal oven	-	anthracite	5.0 kg/tonne
	-	bituminous	7.5 kg/tonne
oil central heating	-	.3 kg/kL	

5.6 Residential Wood Combustion

5.6.1 Source Description

There are three types of residential wood combusters: wood stoves, fireplaces and furnaces.

Residential wood stoves are primarily used as space heaters to supplement conventional heating systems. Commonly made of cast iron, heavy gauge sheet metal and/or stainless steel, there are two main types of wood stoves. Radiating wood stoves transfer heat by radiation from the hot stove walls to the room. Circulating stoves have double wall construction with louvers on the exterior wall. This allows the conversion of radiant energy to warm convection air. The degree of combustion and heat transfer for both types of stoves largely depends on the firebox temperature, residence time and turbulence (mixing). Many stoves have internal baffles which promote heat transfer by increasing the residence time of flue gases. The use of baffles and pre-heated secondary combustion air helps to reduce emissions by promoting mixing and more thorough combustion. (U.S. EPA 1985)

Emissions control for wood stoves may be accomplished in two main ways: operating practices and modified stove design. Operating practices include fuel selection, size, moisture content, feed rate, combustion air supply and equipment maintenance. Design modifications attempt to either reduce pollutant formation in the fuel magazine and/or primary combustion zone or destroy pollutants in the primary or a secondary combustion zone. Catalytic converters, similar to those used in automobiles, are under development for emissions control, but there are difficulties with safely achieving adequate catalyst operating temperatures and there are indications that under certain conditions some emissions are increased with these devices. (U.S. EPA 1985)

There are two main types of fireplaces: masonry fireplaces, which are built in-place, typically have large fixed openings to the firebed. Dampers above the firebed limit heat losses when the fireplace is not in use. Some of these fireplaces are designed or retrofitted with doors and louvers to reduce the intake of combustion air during use. Prefabricated fireplaces may be freestanding or "zero-clearance". Both types are commonly equipped with louvers and glass doors to reduce the intake of combustion air. Some are surrounded by ducts through which floor level air is drawn by natural convection and is returned to the room after heating. (U.S. EPA 1985)

No emissions control devices are available for fireplaces. Fireplace design can reduce emissions by promoting a fast burn rate and higher flame intensity, thereby enhancing secondary combustion (U.S. EPA 1985).

5.6.2 Emission Factors

Emissions from the residential combustion of wood include organics resulting from the combination of free radical species formed in the flame zone, primarily as the result of incomplete combustion. Wide ranges of emission factors for PAH's, PCDDs and PCDFs have been reported. Some of this variability may be attributable to the different conditions under which emissions were measured, including factors such as:

- facility design and degree of excess air
- wood type, moisture content and other wood characteristics
- burn rate and stage of burn
- firebox and chimney temperatures
- sampling and analytical methods

Table 5.6.1 summarizes available PAH emission factors for wood stoves, fireplaces and wood furnaces. Table 5.6.2 provides PCDD AND PCDF concentrations in particulate/soot emissions from residential wood

combustors. Details are provided in notes appended to these tables. PCDD and PCDF emission factors (particulates only) for residential wood combustors based on particulate emission rates from AP-42 (U.S. EPA 1985) are presented in Table 5.6.3. These factors should be considered to represent maximum emission rates for these units, as chimney soot is not necessarily representative of particulate emitted to the atmosphere.

5.6.3 Inventory Comments

The average emission factors, in mg/tonne, in Tables 5.6.1 (PAHs) and 5.6.3 (particulate PCDDs and PCDFs) were used to inventory residential wood combustion as area sources under the following master sector codes:

20501	-	Stoves
20502	-	Fireplaces
20503	-	Wood Furnaces

In Ontario, total residential wood combustion in tonnes was available on the UTM grid. This was broken down into 80% stove and 20% fireplace use, based on data available from a preliminary assessment of wood burning emissions in Ontario (Ontario Research Foundation 1984). The data was available on the UTM grid.

For Canada (other), data was available in the three categories. Base quantities were using NAPAP TSP emission factors and TSP emissions. Total dwellings was used as a spatial allaocation surrogate, as data was only available on a provincial basis.

For the U.S., TSP emission rates and TSP emission factors from NAPAP were used to back calculate total residential wood combustion on a county basis. This was broken down into stove and fireplace use using state specific data for the year 1976 (Versar 1989).

State temporal factors for residential wood use were available in the U.S. NAPAP area files for SCC 006. This was used for both stoves and fireplaces on a state-by-state basis. Michigan temporal factors were used for Ontario and Canada (other).

TABLE 5.6.1

PAH Emission Factor Summary for Residential Wood Combustion (mg/kg wood burned)

	Wood Stoves	Fireplaces	Wood Furnace
Acenaphthene	5.4 (2.2-8.1) de	1.2 d	
Acenaphthylene	21.6 (4.2-64.0) de	10 d	
Anthracene	4.3 (1.1-6.0) abc	8.8 (6.8-11.3)* i	26.2 (20.5-31.9) k
Benzo(a)anthracene	.25 (.06-.44) cd	1.9 d	17.1l
Benzofluoranthenes	13.0 (11.3-14.9) di	1.8 (1.4-2.2) d	
Benzo(a)fluorene	0.3 (.2-.39) cf		
Benzo(ghi)perylene	2.1 (.04-5.9) bcd	1.4 i	
Benzo(a)pyrene	1.2 (.37-3.6) bcdgh	.9 (0.6-1.7) bdhj	23.9 k
Benzo(e)pyrene	0.4 (.23-.5) bc		
Chrysene	1.6 b		
Coronene	<.017b		
Cyclopenta(cd)pyrene	6.5 (.4-12.7) ci		
Dibenz(ah)anthracene	<.017 b		
Dibenzanthracenes	1 d		
Fluoranthene	10.7 (0.2-33.4) efi	1.9 (1.4-2.6) di	31.0 (17.8-54.6) l
Fluorene	7.9 (1.9-20) abde	4.7 d	19.0 (9.3-23.9) l
Methylanthracenes/ Methylphenanthrenes	28.8 (2.9-52) i	3.0 (2.7-3.3) i	
Methylphenanthrenes	16.5 (15.0-19.2) bc		15.3 (11.9-18.6) l
Perylene	.5 (.2-.8) bc		
Phenanthrene	8.2 (5.0-9.8) abc	see anthracene	43.8 (31.9-54.6) l
Pyrene	7.9 (2.1-19.0) bcd	1.9 (1.4-2.6) di	33.6 (17.1-58.1) l

*includes phenanthrene

TABLE 5.6.1 (contd.)

PAH Emission Factor Summary for Residential Wood Combustion (mg/kg wood burned)

Notes

a Truesdale 1984. Represents total baghouse-controlled emissions, results of two emission tests.

b Smith 1984. Literature Review.

c Ramdahl et al 1982. Represents uncontrolled total, results of 6 emission tests over varying wood types and normal and starved air conditions in baffled wood stoves.

d Cooper 1980. Literature Review.

e Knight et al 1983. Average uncontrolled total, tested over a range of wood loads and damper settings. All PAH's found to be in a gaseous phase, except for one test in which particulate PAHs were found.

f Peters 1982. Uncontrolled total emissions.

g Alfheim and Ramdahl 1984. Represents total, results for 4 tests over varying wood types and normal and starved air conditions.

h Ramdahl et al 1981. Literature review of limited database, including DeAngelis et al, 1980.

i DeAngelis et al 1980, Hall and DeAngelis 1980, Hartman and Rives 1985, Peters et al 1981. Represents uncontrolled total emissions.

j Energy and Environmental Analysis Inc. 1978. Represents average total PAH emissions from fireplaces tested burning various woods under stable conditions.

k Truesdale 1984. Represents total PAH emitted by an uncontrolled fluidized-bed home heating furnace.

l Truesdale 1984. Represents total PAH, averaged over tests of uncontrolled and baghouse-controlled emissions from fluidized-bed home heating furnaces.

TABLE 5.6.2

Average (and Range) Concentrations of PCDD and PCDF in Particulate/Soot Emissions from Residential Wood Combustors (µg/kg particulate)

Compound	Wood Stove	Fireplace	Wood Furnace
Dioxins			
T_4CDD-2,3,7,8	.22 (ND-2.23) ac	1.0 d	.135 (ND-.476) ac
T_4CDD	4.10 (ND-25.7) abc	ND b	11.2 (.002-50.5) ac
P_5CDD	23.4 (ND-210) bcd	22.1 (.5-44.7) bd	21.2 (3.65-38.4) c
H_6CDD	10.3 (ND-106) abc	1.7 b	12.4 (.003-65.3) ac
H_7CDD	8.20 (.0125-59.5) abc	.5 b	17.2 (.013-71.8) ac
O_8CDD	7.28 (.024-40.2) abc	.4 b	21.2 (.024-111) ac
Furans			
T_4CDF-2,3,7,8	9.37 (.037-33.5) c	not available	11.3 (6.18-18.1) c
T_4CDF	68.7 (ND-321) bc	0.3 b	163 (90.5-205) c
P_5CDF	81.9 (ND-499) bc	1.4 b	260 (183-409) c
H_6CDF	51.2 (ND-399) bc	1.7 b	77.0 (61.9-94.4) c
H_7CDF	12.0 (ND-91.6) bc	0.4 b	13.8 (10.2-20.3) c
O_8CDF	6.8 (ND-60.6) bc	0.1 b	2.83 (2.01-4.38) c

a Nestrick and Lamparski 1982. All particulate samples were obtained from residential wood combustion unit chimneys (n=18) for each of woodstove and wood furnaces). Six individual samples were taken from each of three rural regions of the United States. The wood used for these tests had not been treated with or exposed to 2,4-D, 2,4,5-T or pentachlorophenol.

b Clement et al 1985. Samples of chimney ash were collected from two wood burning stoves and one open fireplace.

c Thoma 1988. Chimney soot samples were collected from 4 wood furnaces (wood central heating) and 9 wood ovens (stoves) in the area of Bayreuth, Germany.

d U.S. EPA (1987e). Data given is based on Nestrick and Lamparski 1982.

TABLE 5.6.3

Particulate PCDD and PCDF Emission Factors for Residential Wood Combustion (mg/tonne wood burned)*

	Wood Stove	Fireplace	Wood Furnace
Dioxins			
T_4CDD-2,3,7,8	.0046	.014	.0027
T_4CDD	.086	0	.24
P_5CDD	.49	.31	.44
H_6CDD	.22	.024	.26
H_7CDD	.17	.0070	.36
O_8CDD	.15	.0056	.45
Furans			
T_4CDF-2,3,7,8	.20	not available	.24
T_4CDF	1.4	.0042	3.4
P_5CDF	1.7	.020	5.5
H_6CDF	1.1	.024	1.6
H_7CDF	.25	.0056	.29
O_8CDF	.14	.0014	.059

* Based on average emission factors presented in Table 5.6.2 and particulate emission rates from AP-42 (U.S. EPA 1985) as follows:

- wood stove - 21 kg/tonne
- fireplace - 14 kg/tonne
- wood furnace - 21 kg/tonne (assumed to be identical to wood stove)

5.7 Internal Combustion Sources

5.7.1 Source Description

Internal combustion sources include a wide variety of fuels, equipment designs and applications. A U.S. EPA review of internal combustion sources (Shih et al 1979) identified gas turbines and reciprocating engines for electricity generation and industrial applications as having the most potential of the internal combustors for significant emissions of criteria and selected other pollutants.

Gas turbines include simple open cycle, regenerative open cycle and combined cycle turbines. The regenerative open cycle type is a very small portion of the total turbine population and emissions from identical gas turbines used in the combined cycle and in the simple cycle are identical. Therefore, the U.S. EPA study (Shih et al 1979) evaluated only emissions from simple cycles. Simple cycle gas turbines may be natural gas-fuelled or distillate oil-fuelled (diesel).

Reciprocating engines are either spark ignition (gasoline-fuelled) or compression ignition (diesel-fuelled). Spark ignition engines are rarely used for electricity generation or industrial applications because of their poor part-load economy and cost of fuel. Therefore, the U.S. EPA measurement program focussed on diesel-fuelled reciprocating engines (Shih et al 1979).

Principal applications of these internal combustion sources are listed in Table 5.7.1.

Air emissions control equipment is not usually installed on gas turbines or reciprocating engines (Shih et al 1979).

5.7.2 Emission Factor

The U.S. EPA study of emissions from internal combustion engines for industrial applications and electricity generation (Shih et al 1979) involved a critical examination of existing emissions data, followed by a measurement program designed to fill data gaps based on a phased sampling and analysis strategy.

For gas turbines the only existing data found was from a study from Hurley and Hersh (1977) presented in Table 5.7.2. However, this data was questionable, as the highest POM levels obtained were from an ambient air sample. In the measurement phase of the U.S. EPA program, one gasoline-fuelled and five diesel-fuelled gas turbines were tested. POM emissions from these engines could not be differentiated from the blank values. Table 5.7.2 lists the PAH's of interest to this study that were looked for, but not detected in the samples.

No existing data was found in the U.S. EPA study (Shih et al 1979) for diesel-fuelled reciprocating engines. In the measurement phase of the program, five diesel-fuelled reciprocating engines were tested for organic emissions. The results indicated that organic emissions from these engines consist mainly of saturated and unsaturated aliphatic and aromatic hydrocarbons. Table 5.7.3 presents the results for PAH's of interest to this inventory. These results are for eight emissions tests conducted at five sites.

Table 5.7.4 lists emission factors (averages and ranges) for industrial applications and electricity generation for gas turbines and reciprocating engines. These emission factors were based on data presented in Tables 5.7.2 and 5.7.3, using conversion factors from AP-42 (U.S. EPA 1985).

Heavy duty gasoline powered vehicle PAH emission factors were used for gasoline-fuelled reciprocating engines (see Section 7.1). Heavy duty diesel powered vehicle PAH emission factors were used for diesel-fuelled large bore engines (see Section 7.2).

No PCB, PCDD or PCDF emissions data were found for internal combustion sources.

5.7.3 Inventory Comments

The emission factors discussed in Section 5.7.2 were used to inventory point (P) and area (A) internal combustion sources using base quantity data from NAPAP as follows:

Description Master Sector Code	Ontario	Can. (other)	U.S.
Diesel Turbines 20701	-	P	P
Diesel Reciprocating 20702	-	P,A	P
Diesel Large Bore 20703	-	-	P
Gasoline 20704	-	-	P

Point sources with non-zero base quantities were taken from NAPAP files. For Master Sector Codes 20703, 20704, base quantities had to be converted into VKmT using 93.3 km/U.S. gal. for gasoline and 9.7 km/U.S. gal. for diesel, in order to match the emission factor units. This approach is no different than converting the vehicular emission factors into a fuel usage basis using fleet average fuel efficiencies. All points have point specific

temporal factors. These points may come from various sectors, such as utilities, industrial and commercial/institutional fuel combustion, but are grouped together under internal combustion.

The Canada (other) area source is from miscellaneous power generation. Base quantities were derived from NAPAP TSP emissions and emission factors on a provincial basis. Industrial labour force was used as a spatial allocation factor. This was assumed to have no temporal variation.

TABLE 5.7.1

Principal Applications of Utility and Industrial Internal Combustion Engines (Durkee et al 1977)

Type	Size Category	Principal Applications
Gas Turbines	<1,000 HP	Compressor and pump drive, standby electricity generation
	1,000-5,000 HP	Oil and gas transmission, natural gas processing, standby electricity generation, private industry electricity generation, compressor and pump drive
	5,000-20,000 HP	Oil and gas transmission, natural gas processing, standby electricity generation, private industry electricity generation
	>20,000 HP (~15 MW)	Peak load electricity generation
	Combined cycle >100 MW	Base load electricity generation
Reciprocating Engines	400-1,000 HP (Medium engines)	Oil and gas production and exploration, natural gas processing, compressor and pump drive, private industry electricity, standby electricity generation
	>1,000 HP (Large engines)	Oil and gas transmission, natural gas processing, peak load and base load electricity generation, nuclear standby power

TABLE 5.7.2

PAH Emission Data for Gas Turbine Internal Combustion Engines (pg/J)

	Gas-Fuelled[1,2]	Diesel-Fuelled[5]				
		Hurley and Hersh (1977)				U.S. EPA[1,3] (Shih et al 1979)
		No Additive	Mn Additive	Ba/Mn Additive	Fe Additive	
Anthracene/Phenanthrene	N.D.[6]	1.53	1.36	1.37	2.36	N.D.
Benzo(a)anthracene	N.D.					N.D.
Benzofluoranthenes	N.D.	N.D.	N.D.	N.D.	.06	N.D.
Benzo(b)fluoranthene	N.D.					N.D.
Benzo(f)fluoranthene	N.D.					N.D.
Benzo(k)fluoranthene	N.D.					N.D.
Benzo(a)fluorene	N.D.					N.D.
Benzo(ghi)perylene	N.D.					N.D.
Benzo(a)pyrene	N.D.	N.D.	N.D.	N.D.	.03	N.D.
Benzo(e)pyrene	N.D.	N.D.	N.D.	N.D.	.06	N.D.
Chrysene	N.D.	0.06[4]	N.D.[4]	N.D.[4]	.18[4]	N.D.
Coronene	N.D.					N.D.
Dibenzothlophene	N.D.					N.D.
Fluoranthene	N.D.	0.23	0.24	0.25	0.52	N.D.
Fluorene	N.D.					N.D.
Methylanthracenes	N.D.	0.95	0.84	0.66	1.03	N.D.
Methylphenanthrenes	N.D.					N.D.
Perylene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Pyrene	N.D.	0.10	0.14	0.12	0.46	N.D.
Triphenylene	N.D.					N.D.

1 Tested in measurement phase of a U.S. EPA assessment program (Shih et al 1979). Electricity generation engines were tested, ranging from 80 to 100 percent of base load.
2 One site tested.
3 Five sites tested. Detection limits ranged from .03 to .05 pg/J.
4 Represents chrysene/benz(a)anthracene
5 Electricity generation turbine operating at 70 percent of base load.
6 ND = not detected

TABLE 5.7.3

PAH Emission Data for Diesel-Fuelled Reciprocating Internal Combustion Engines (Shih et al 1979)* (pg/J)

	Mean	Range
Anthracene/Phenanthrene	19.1	N.D.-68.6
Benzo(a)anthracene	N.D.	
Benzofluoranthenes	N.D.	
Benzo(b)fluoranthene	N.D.	
Benzo(f)fluoranthene	N.D.	
Benzo(k)fluoranthene	N.D.	
Benzo(a)fluorene	N.D.	
Benzo(ghi)perylene	N.D.	
Benzo(a)pyrene	N.D.	
Benzo(e)pyrene	N.D.	
Chrysene	N.D.	
Coronene	N.D.	
Dibenzothiophene	.50	N.D.-2.6
Fluoranthene	N.D.	
Fluorene	N.D.	
Methylanthracenes	N.D.	
Methylphenanthrenes	48.8	N.D.-141.5
Perylene	N.D.	
Pyrene	N.D.	
Triphenylene	N.D.	

N.D. Not detected

* Data for 5 sites, 8 emission tests. Electricity generation engines were tested. All tests at 100% of base load. Detection limits ranged from .03 to .05 pg/J. PAH's were found only in the vapour phase.

TABLE 5.7.4*

PAH Emission Factors for Internal Combustion Engines Industrial and Electricity Generation (mg/kl)

	Gas Turbines		Reciprocating Engines
	Gas-Fuelled	Diesel-Fuelled	Diesel-Fuelled
Anthracene/Phenanthrene	0	5.0 (0-16.0)	130 (0-470)
Benzo(a)anthracene	0	0	0
Benzofluoranthenes	0	.05 (0-.4)	0
Benzo(b)fluoranthene	0	0	0
Benzo(f)fluoranthene	0	0	0
Benzo(k)fluoranthene	0	0	0
Benzo(a)fluorene	0	0	0
Benzo(ghi)perylene	0	0	0
Benzo(a)pyrene	0	.03 (0-.2)	0
Benzo(e)pyrene	0	.05 (0-.4)	0
Chrysene	0	.18 (0-1.2)	0
Coronene	0	0	0
Dibenzothiophene	0	0	3.4 (0-18)
Fluoranthene	0	.94 (0-3.5)	0
Fluorene	0	0	0
Methylanthracenes	0	2.6 (0-7.0)	0
Methylphenanthrenes	0	0	330 (0-960)
Perylene	0	0	0
Pyrene	0	.62 (0-3.1)	0
Triphenylene	0	0	0

* Based on Tables I.2 and I.3, using conversion factors in AP-42 (U.S. EPA 1985).

6. SOLID/LIQUID WASTE INCINERATION

6.1 Municipal Waste Incineration

6.1.1 Process Description

With major growth in the use of incineration to reduce waste volumes and opportunities to recover energy, there is increased public concern regarding potential emissions from centralized facilities. On the basis of available emission estimates and other studies, incineration of municipal solid waste is deduced to be a substantial anthropogenic source of PCDD and PCDF emissions to air relative to several other source categories (MOE 1984a, Sheffield 1985, Czuczwa and Hites 1986). As for other combustion sources, these constituents, along with PCB and PAH, occur at trace concentrations or represent only very minor components of incinerator stack emissions. It has been estimated that municipal refuse is generated at a per capita rate of 1.8 kg/day (Klicius 1987) and household refuse typically comprises 25-50% paper, 10-50% food waste and other organic materials, 3-10% metals, 3-9% glass and 7-25% other non-combustibles (Alter 1987, Ozvacic et al 1985). Although there is uncertainty with respect to the formation mechanisms of trace organic constituents such as dioxins during combustion, the following factors are reported (Keating 1986, McInnes and Hunt 1986) to affect the magnitude of such emissions:

- component or precursor content of the feed (e.g., chlorine-containing species such as chlorobenzenes, chlorophenols, PCBs),
- type and extent of feed processing (e.g., removal of non-combustible material, shredding or pelletizing refuse),
- combustion and operating conditions (e.g., temperature, residence times, oxygen availability),
- type of incinerator and supplementary fuel,

- type and removal efficiency of the associated emission control device including use of heat recovery.

The types and features of several Canadian, U.S. and European incinerator facilities have been described and emissions have been documented in varying levels of detail (U.S. EPA 1987a, U.S. EPA 1987e, U.S. EPA 1987f, McInnes and Hunt 1986, Beychok 1987, Seibert et al 1987, Voldner and Ellenton 1987, U.S. EPA 1989). Emissions data have also been normalized, where possible, to allow better comparisons to be made between facilities for risk assessment purposes. The major types of known MSW incinerators in the U.S. and presently estimated relative population and waste combustion capacities (U.S. EPA 1989) are shown below:

MSW Incinerator Type	Fraction of Population	Fraction of Waste Burning Capacity
Mass Burn	37%	58%
Modular	43%	9%
RDF-Fired	12%	29%
Fluidized Bed or Unknown Configuration	8%	4%

The majority of planned U.S. facilities (i.e., commence construction in 1989) are mass burn (waterwall) designs and a substantial total increase of incinerators is planned (i.e., estimates of 161 existing and 111 new facilities)

Refractory-wall mass burn combustors are generally older units (built prior to the early 1970's) that burn unprocessed wastes and consist of single or multiple rectangular chambers in which waste enters by batch or continuous feed and moves through the chambers by travelling, rocking or reciprocating grate systems. Refractory-lined rotary kilns are also included in this category. Both older and modern mass burn waterwall facilities utilize gravity or hydraulic ram feeders and move uncompressed wastes through the

combustion chambers by reciprocating grates. A few rotary waterwall combustion chambers also exist. Most of the mass burn facilities use ESP particulate control devices and some older units use scrubbers. In addition, several newer units control acid gases with wet scrubbers, spray dryers or dry sorbent injection. Modular combustors are classified as starved-air or excess-air designs with several common features. Usually, they are smaller construction batch-fed without waste pre-processing and consist of two refractory-lined chambers whereby air is introduced to the primary chamber at either below stoichiometric requirements or in excess amounts according to the design. Most starved-air units use auxilliary fuel burners for startup or maintaining temperature when necessary. Emission control devices are not normally used on modular incinerators. Refuse-derived fuel-fired incinerators burn processed wastes (i.e., shredded or finely divided for co-firing with coal) and usually recover heat from the boiler for producing steam or electricity. RDF systems generally have ESP controls and may have acid gas spray dryer systems. A small fraction of waste is also estimated to be burned in fluidized-bed combustion units or other technologies in which pelletized waste is suspended with non-combustible material in a chamber with underfire air. Only minimal emissions data exist for the latter combustion designs.

6.1.2 Emission Factors

A significant amount of North American source testing information is available for MSW incinerators with most recent focus on trace organic assessments. However, it is sometimes difficult, without sufficient reported data, to compare the wide-ranging emissions for some of the facilities tested and derive average emission factors in units of contaminant mass per mass of refuse incinerated. Similarly, because of the variability of waste composition and differences between facilities, control equipment efficiencies and operating practices, emission factors can vary significantly between individual facilities and for individual tests conducted on the same

incinerator. Emission factors, that have been reported or derived from source test data, are presented in Table 6.1.1 for the various types of MSW incinerator technologies. Because most of the conventional incinerators are controlled by ESPs (~75%) or wet scrubbers (~20%) (U.S. EPA 1987a), controlled emission factors are tabulated. Many of the emission factors were obtained from recent reports prepared for U.S. EPA (U.S. EPA 1987a, U.S. EPA 1987f, U.S. EPA 1989), whereby facility emissions were selected and averaged on the basis of common factors and normal operation. In some instances, measurement data from three facilities in Canada have been combined (Ozvacic et al 1985, Hay et al 1986, MOE 1984b, Thorndyke 1986). Of note, emission factors have recently been reported (U.S. EPA 1989) for total PCDDs and PCDFs, the 2,3,7,8 TCDD and TCDF isomers and the total TCDD and TCDF congeners. In order to expand these data to emission factors for all congeners, average congener profiles were derived from direct source test information (McInnis and Hunt 1986, U.S. EPA 1987f). Where possible, the profiles for the identical sources were used but, in some instances, results for one or more similar facilities were combined in the averages. On occasion, an emission factor for a single test is included. Emission factors for the speciated PAH compounds primarily represent averages for mass burn facilities, based upon U.S. measurements (U.S. EPA 1987a) which have been reported elsewhere (Johnson 1989). However, insufficient information was available to classify these to the specific type of incinerator unit. As noted earlier, some wide variations in some of the emission factors exist, due presumably to feed and operational differences between facilities.

TABLE 6.1.1

Municipal Solid Waste Incineration Emission Factors

Pollutant	Controlled Emission Factor (mg/Tonne Refuse) by Facility Type[1]					
	Mass Burn Refractory Wall	Mass Burn Waterwall	Mass Burn Waterwall Old Units[2]	Modular Starved or New Units	RDF Units Excess Air[3]	Various Types[4]
Tot. PCDD	12	12	0.50	0.47	2.9	
2,3,7,8 T_4CDD	0.004	0.01	0.001	0.002	0.009	
T_4CDD	0.9	1.7	0.055	0.038	0.37	
P_5CDD	2.2	4.0	0.065	0.062	0.55	
H_6CDD	5.3	2.9	0.10	0.11	0.67	
H_7CDD	2.5	2.7	0.12	0.13	0.90	
OCDD	1.1	0.7	0.16	0.13	0.41	
Tot. PCDF	13	24	0.69	0.45	1.7	
T_4CDF	3.2	6.7	0.29	0.08	0.59	
P_5CDF	2.9	9.2	0.15	0.11	0.55	
H_6CDF	4.6	6.5	0.14	0.13	0.26	
H_7CDF	2.1	1.5	0.10	0.11	0.26	
OCDF	0.2	0.1	0.01	0.02	0.04	
Tot. PCB	4.5	2.7		2.5	1.3	
Tot PAH						1,200
Acenaphthene						12
Acenaphthalene						1,000
Benz(a)anthracene + Chrysene						3.1
Benzofluoranthenes						78
Benzo(ghi)perylene						14
Benzo(a)pyrene		4.8		3.1	130	24
Chrysene						62
Coronene						0.02
Dibenz(ah)anthracene						0.1
Fluoranthene						140
Fluorene						63
Indeno(1,2,3-cd)pyrene						0.8
Perylene						0.8
Phenanthrene						430
Pyrene						170

Notes:

1. Generally emission factors represent facilities controlled by ESPs except for modular units which are uncontrolled. Principal references include EPA 1987a and EPA 1989.
2. Old units are considered to be those built prior to the early 1970's.
3. Minor emission factor differences exist for starved and excess air facilities.
4. Primarily, reflect emission factors for mass burn facilities.

6.2 Sewage Sludge Incineration

6.2.1 Source Description

Several of the components of concern are emitted during incineration of sewage sludge. Approximately 50% of the estimated sewage sludge generated in Ontario is incinerated at six municipal facilities (MOE 1985). Two other sewage sludge incinerators exist in other provinces. Most are multiple hearth systems with emissions controlled by wet scrubbers and some are fluidized bed units with scrubber control systems. Approximately 156 sludge incinerators operated in the U.S. as of 1985, comprising 120 multiple hearth, 25 fluidized bed and 11 other facilities (e.g., electric, rotary kiln and co-combustion technologies) (Science Applications International Corp. 1987). A somewhat larger estimate of U.S. facilities has also been reported but with similar proportions of facility types (EPA 1987a). Several toxic chemical components (e.g., PCB, PCDD, PCDF and various pesticides) have been analyzed in sewage sludge in various countries and these can be partially emitted or destroyed during incineration (Furr et al 1976, Mumma et al 1983, McIntyre and Lester 1984, MOE 1985). It has been suggested that the PCDD/PCDF content of the sludge may partly account for the measured emissions (Sheffield 1985). Similarly, it was suggested that the design of the commonly-used incineration systems may promote evaporation of some feed components, such as low molecular weight PCB, rather than combustion of these species (Murphy 1982).

As described in various reports (e.g., Science Applications International Corp. 1987), the multiple hearth incinerator is a counter-current vertical combustor with the cylindrical furnace shell divided into 6 to 12 hearths. A central rotating shaft contains rabble arms attached at each hearth level which forces the coke to the next lower level. The furnace consists of three zones: sludge drying by the hot combustion gases upon entry, sludge burning in the combustion zone, and the cooling zone whereby hot sludge

ash warms the combustion air that enters the furnace. Flue gases, that exit the top of the furnace, are directed to a scrubber and ash discharges from the bottom of the furnace. Fluidized bed incinerators are usually single chamber vertical furnaces containing a sandbed which results in mixing (or fluidizing) of sludge and sand by combustion air that enters the furnace bottom. The less dense sludge ash is carried out of the furnace with flue gases to a Venturi scrubber and secondary wet scrubber.

6.2.2 Emission Factors

Semi-volatile organics have been measured in emissions of several multiple hearth furnaces which represent the primary type of sewage sludge incinerators. Controlled emission factors are shown in Table 6.2.1. Many of the PAH emission factors are based on recent measurements at two Ontario sewage sludge incinerators and some PAH constituents were derived from two other facilities in Ontario and the U.S. (Thorndyke 1989a and b, Environment Canada 1983c, PEI Associates 1986). Emission factors for PCDD, PCDF and PCB were averaged, based on source measurements conducted at three Canadian and three U.S. facilities (Thorndyke 1989a and b, U.S. EPA 1987e, Murphy et al 1985, Thorndyke 1980, Environment Canada 1983c). Although various pesticides may be present in the incinerator sludge feed, the following pesticides were not detected in controlled emissions of four incinerators tested: aldrin, chlordane, dieldrin and toxaphene (Crumpler et al 1988). It should be noted that the average PCDD and PCDF emission factors utilized for sewage sludge incineration in this study are somewhat lower than the factors used in earlier Ontario and Canadian emission estimates (MOE 1985, Sheffield 1985).

TABLE 6.2.1

Sewage Sludge Incinerator - Emission Factors

Pollutant	Controlled Emission Factor[1] (mg/Tonne Dry Sludge Burned)	Range[2]
Total PCDD	0.20	0.005-0.62
2,3,7,8 T_4CDD	0.00049	0.00022-0.00094
T_4CDD	0.05	0.0043-0.15
P_5CDD	0.01	0.00005-0.04
H_6CDD	0.03	0.0005-0.11
H_7CDD	0.06	0.009-0.23
O_8CDD	0.04	0.003-0.11
Total PCDF	0.73	0.030-3.0
T_4CDF	0.33	0.010-1.2
P_5CDF	0.21	0.010-0.72
H_6CDF	0.04	0.002-0.15
H_7CDF	0.05	ND-0.27
O_8CDF	0.04	ND-0.18
Total PCB	5.4	0.69-14
Total PAH	127	
Acenaphthene	0.23	0.022-0.43
Acenaphthylene	0.004	0.0017-0.0069
Anthracene	0.08	0.014-0.14
Benz(a)anthracene	0.62	0.018-1.2
Benzo(b)fluoranthene	0.07	0.07
Benzo(k)fluoranthene	0.61	0.52-0.70
Benzo(a)fluorene	0.88	0.31-1.4
Benzo(a)pyrene	0.51	0.26-1.0
Benzo(e)pyrene	0.47	0.22-0.72
Benzo(ghi)perylene	0.04	0.008-0.062
Chrysene/Triphenylene	7.2	4.3-9.9
Coronene	0.04	ND-0.074
Fluoranthene	62	4.4-190
Fluorene	4.4	1.4-9
Indeno(1,2,3-cd)pyrene	0.10	0.024-0.18
Methylanthracenes	0.09	0.004-0.17
Methylphenanthrenes	3.9	32.4-4.5
Perylene	0.03	0.003-0.067
Phenanthrene	44	19.6-90
Pyrene	1.8	0.16-3.43

Notes:

1. For multi-hearth incinerators controlled by wet scrubbers
2. Average emission factors and ranges based on the following sets of measurements by compound class (i.e., number of separate incinerators tested with test set results averaged in each): PCDD-6 incinerators tested, PCDF-6 incinerators tested, PCB-5 incinerators tested, PAH-mainly 2 and occasionally 3 incinerators tested.

6.3 Industrial Waste Incineration

6.3.1 Processes

With legislative tendencies toward reduction or treatment of wastes at the source in order to minimize traditional landfilling, it is anticipated that growth will occur in the use of industrial waste incineration and other thermal destruction methods (Oppelt 1987). The major types of on-site or centralized facilities to destroy either solid or liquid industrial wastes include:

- fixed hearth incinerators (usually two stage)
- packaged incinerators
- rotary kiln incinerators
- reclamation furnaces
- conical burners for wood wastes
- liquid injection incinerators
- gas or oil-fired water tube boilers for waste co-firing

Such industrial waste combustors are often manually charged and intermittently operated with feed rates that may range from 20 to 1800 kg/hour (U.S. EPA 1988b). Factors such as the combustor design, waste composition, the operating conditions and control device efficiencies will have a pronounced effect on emissions and emission rates can be expected to vary widely between facilities.

Industrial solid wastes combusted in incinerators are reported to consist primarily of process wastes and industrial refuse that contain paper, plastic, rubber, textiles and wood (U.S. EPA 1987a). Waste composition can be expected to be highly variable between plants. In the U.S., most industrial incinerators are dual or multichamber designs (91%), some are single chamber (9%) and most are equipped with afterburners while newer units may have scrubbers or ESPs. It has been estimated that of the ~3800 industrial incinerators in the U.S., approximately 1500 are used for waste volume reduction primarily by industries such as: lumber and wood producers, primary metals and printing (U.S. EPA 1987a). Of the remaining units, approximately 1700 are used for resource recovery (primarily at copper wire and electric motors plants) and 640 units for toxicity reduction (mainly at petroleum and chemical industries). No reports have been found that characterize industrial waste incineration in Canada. Similarly, the amount of waste incinerated by industry is not well-established. Environment Canada uses a throughput ratio developed by EPA of 9 tonnes of industrial/commercial waste to 16.6 tonnes of municipal waste (Environment Canada 1986b).

Liquid industrial wastes are usually incinerated with primary fuels in facilities such as: two staged incinerators, controlled air packaged incinerators or co-fired in industrial waterwall boilers. Liquid wastes with some calorific value that are typically incinerated include: solvents, oils, organic by-products and sludges. These may be injected directly into a furnace chamber by spraying or atomized in a primary fuel burner. In most instances, the incinerator facilities are capable of efficiently destroying the organic content of the feed but trace organics (e.g. products of incomplete combustion and contaminants formed during combustion) may be present in emissions. Industrial boilers co-firing wastes are often uncontrolled, as evident from several U.S. facilities that have been tested (Accurex 1986). On the other hand, some industrial waste incineration facilities are controlled with a scrubber or baghouse.

Wigwam or conical burners, associated with lumber, plywood and other forest product mills, are still used in some remote areas in Ontario and elsewhere to dispose of wood wastes. Some of these wastes may be burned in boilers to generate power at the sawmill or transported to nearby pulp and paper mills, where feasible, for combustion (see Section 5.3). As noted elsewhere (Environment Canada 1976, Edwards and Cotton 1988), air is blown below the grate and above the fuel pile to maintain combustion of the wood refuse without supplmentary fuel. Due to the generally poor combustion conditions, associated with often poorly maintained burners, such facilities might be expected to represent significant sources of PAH emissions. The extent of particulate control has not been recently documented. Some facilities are equipped with ESPs but most are presumed to be uncontrolled.

Other types of specialized industrial waste incinerators have been examined by U.S. regulatory agencies such as: wire reclamation furnaces, drum and barrel reclamation incinerators and stationary or mobile PCB waste incinerators. For example, emission testing has been conducted on individual metal recovery incinerators as discussed below. However, it is unknown whether these types of incinerators exist in Canada (Sheffield 1985). Incineration of PCB liquid wastes can be accomplished by various types of facilities such as: liquid injection, rotary kiln incinerators or other specialized units (Piersol 1989). As of 1986, in the U.S., four stationary commercial incinerators, eight industrial incinerators and two mobile incinerators were approved to burn PCB liquids (U.S. EPA 1987h). The extent to which these facilities have been used was not reported. It has been estimated that ~5% of the total amount of PCBs produced or distributed in the U.S. had been destroyed by treatment facilities by 1987 (U.S. EPA 1987h). None of these PCB destruction facilities have been utilized in Canada.

6.3.2 Emission Factors

Because there are numerous types of industrial wastes that may be incinerated as well as several incinerator configurations and operating modes, an accurate definition or prediction of emission rates for this sector is difficult. Emission factors for various types of industrial waste incineration activities are shown in Table 6.3.1. In some instances, these were based on direct emission measurements from a single facility, reported in other studies or estimated based on emissions from similar facilities. Dioxin and furan emission factors have been determined from source testing at three different types of U.S. industrial incinerators (U.S. EPA 1987e). For example, the PCDD and PCDF emission factors are shown for a two-chamber, controlled air incinerator with an oil-fired afterburner which incinerated wastes containing pentachlorophenyl-treated wood wastes, polyvinyl chloride materials, paper and paint sludge. These data might be expected to generally reflect the most common type of industrial incinerators in use and the waste composition is typical of solid wastes incinerated by several industries. The presence of dioxins and furans in ash and stack gases has also been reported for pilot-scale testing of incinerators burning PCP-treated wood such as military ammunition boxes, wood chips, sprayed wood and painted wood or paper (U.S. EPA 1987e, Sheffield 1985, Keating 1986). Of further note, European data on combustion of paper recycling residues have indicated a pronounced increase in emissions of the lower chlorinated homologs (i.e. TCDD and TCDF) with increased amounts of paper recycling residues (Scheidl et al 1986). With low paper residue content, the relative homolog distributions of these emissions were similar to those shown for the solid waste incinerators. Although PAH emissions might also be expected from such facilities, few measured data exist. Accordingly, PAH emission factors based on a packaged, controlled-air commercial incinerator burning municipal refuse (U.S. EPA 1987a) were applied to industrial mixed solid waste incinerators.

The emission factors for mixed liquid industrial waste shown in Table 6.3.1 are based on comprehensive emission testing at a single facility in Ontario (Thorndyke 1987). This facility comprises a dual-chamber liquid injection system with scrubber/baghouse emission controls that burns non-PCB containing liquid industrial wastes. No data were found for comparable facilities. On the other hand, stack gas PCDD and PCDF concentration data have been reported for several U.S. industrial boilers that co-fire liquid industrial wastes such as methanol, toluene and various chlorinated solvents in watertube boilers (Accurex 1986). It is noteworthy that PCDD and PCDF concentrations varied considerably between facilities but in several instances, relatively greater stack gas concentrations were found for the lower chlorinated homologs (i.e., tetra and penta homologs). The compound 2,3,7,8-TCDD was rarely detected. It could not be stated with certainty that the measured dioxin and furan flue gas concentrations were generated products of combustion or vapourized from the waste feed (Accurex 1986). Although emission factors could not be determined from these tests (i.e. due to insufficient information regarding waste fuel rates), the relative homolog distributions were, in some cases, similar to those of the tabulated emission factors.

Emission factors for conical or wigwam burners were not found in the information reviewed. Although some criteria pollutant emission testing has been done on a conical burner (Environment Canada 1976), it is doubtful whether PAH emissions have been measured. Because such facilities might represent significant individual sources of PAH, surrogate emission factors have been applied in this inventory as shown in Table 6.3.1. These data are based on reported laboratory stack tests of uncontrolled smoldering fire emissions in which pine needles were the principal fuel (U.S. EPA 1987a). Thus, these emission factors may not adequately represent conical burner emission factors. It should be noted that these are of the same general order-of-magnitude as the emission

factors for residential wood stoves (see Section 5.6) which might also be used as surrogate data for this source.

In addition, PCDD and PCDF emission factors for specialized types of industrial incinerators are shown in Table 6.3.1. Data for the wire reclamation furnace are based on measurements at a dual chamber incinerator with a natural gas-fired afterburner (U.S. EPA 1987e). Tests were conducted during batch burning of PVC-coated copper wire for metal recovery. Ash samples from another wire-reclamation incinerator also were reported to contain TCDD and TCDF (U.S. EPA 1987e). Separate tests on the same facility burning drained PCB-contaminated transformer cores (also containing cardboard, paper and wood components of the cores) resulted in somewhat higher dioxin and furan emission factors than the copper wire burning. Emission factors are also shown for measurements done at a natural gas-fired drum and barrel incinerator with a gas afterburner. Combustible materials in the feed included solvent residues and drum coatings from materials originally contained in the drums such as: lacquer, organic solvents, inks, enamel paints, etc. (U.S. EPA 1987e).

Incineration of liquid PCB wastes is being conducted in the U.S. Concentrations of PCB, PCDD and PCDF have been reported as non-detectable based on stack measurements for high-efficiency boilers while co-firing test amounts of 50-500 ppm PCB contamined mineral oil with conventional fossil fuels (Hunt et al 1984). Similarly, none of these compounds was detected in stack gases at one of the above pulverized coal-fired facilities during a subsequent trial burn with an oil/askarel blend containing 5% PCBs (Siedhoff 1985). Total PCB emission factors for 12 facilities, comprising co-fired liquid injection systems, rotary kilns and mobile incinerators have ranged from 0.02 to 100 mg/kg PCB charged (U.S. EPA 1987h). In most instances, these data are based on research and development rather than compliance testing. Due to the

small extent of PCB incineration which has occurred in North America by 1985, this source of emissions was considered to be minimal.

6.3.3 Inventory Comments

The above mentioned emission factors were applied to appropriate base quantities in the NAPAP file according to SCC descriptors. For example, account of most of the industrial waste burned in the U.S. is contained in point source files such as: solid and liquid waste used in known external combustion boilers, industrial process fuels, electrical winding incinerators and industrial waste disposal in identified incinerators by solid or liquid waste type. A fraction is also assigned to area sources such as on-site industrial incineration. An estimated liquid waste density factor of 0.9 Kg/L was applied in order to convert liquid waste base quantities, in units of U.S. gallons to mass, for compatibility with mass units of the emission factors. Alternatively, most of the Canadian industrial waste base quantities are contained in area source files which represent an estimate only of industrial wastes incinerated. It should be noted that conical wood waste base quantities were not readily distinguished in U.S. files and the extent of this practice is uncertain. Despite MOE efforts to procure base quantity data on industrial waste consumption through questionnaires, it is evident that much of these data are lacking. Data are available for a few point sources only. Hence, total Canadian emission rates for the industrial waste incineration sector are particularly uncertain.

TABLE 6.3.1

Industrial Waste Incineration Emission Factors

Pollutant	Solid Waste (mg/tonne)				Liquid Waste (mg/tonne)
	Mixed Waste[1]	Drum + Barrel Reclamation[2]	Wire Reclamation	Conical or Wigwam Burners[4]	Mixed Waste[5]
Total PCDD	1.70	0.203	0.356		12.3
2,3,7,8 T_4CDD	0.0129	0.0482	0.000283		-
T_4CDD	0.235	0.0503	0.00269		3.9
P_5CDD	0.293	0.0292	0.00623		3.1
H_6CDD	0.401	0.0322	0.0166		4.6
H_7CDD	0.598	0.0534	0.181		0.58
OCDD	0.174	0.0375	0.149		0.18
Total PCDF	6.30	1.10	0.643		4.6
2,3,7,8 T_4CDF	0.0591	0.0365	0.00113	-	
T_4CDF	1.61	0.623	0.0285		1.7
P_5CDF	1.60	0.253	0.0459		1.4
H_6CDF	1.71	0.122	0.0726		0.99
H_7CDF	1.19	0.0822	0.342		0.49
OCDF	0.186	0.0224	0.144		0.03
Total PCB					1.18
Total PAH	2,100			21,000	155
Acenaphthene					3.6
Acenaphthalene					2.7
Anthracene	100			4,100	5.8
Benz(a)anthracene				510	3.0
Benzofluoranthenes				240	2.5
Benzo(ghi)perylene	200				2.1
Benzo(a)pyrene	120			100	1.0
Benzo(e)pyrene	100			150	1.5
Chrysene & Triphenylene				510	5.5
Coronene	50				1.3
Dibenz(ah)anthracene					0.6
Fluoranthene				1,700	24.8
Fluorene	500				6.7
Indeno(1,2,3cd)pyrene					1.9
Methylanthracenes				7,800	18.9
Methylphenanthrenes					8.8
Perylene	10			40	0.3
Phenanthrene	310			4,100	50.2
Pyrene	700			1,900	14

TABLE 6.3.1 (Contd.)

Industrial Waste Incineration Emission Factors

Notes:

1. Based on tests at a dual chamber controlled air incinerator with an oil-fired afterburner burning PVC, PCP-treated wood waste, paint sludges, paper, etc. PAH emission factors were based on a packaged, controlled-air commercial incinerator burning municipal refuse.

2. Based on tests at a semi-continuous feed incinerator with a natural gas afterburner for reclaiming barrels containing lacquers, solvents, paint residues, etc.

3. Based on tests at a dual chamber wire reclamation furnace with a natural gas afterburner for batch burning of PVC-coated copper wire.

4. Based on laboratory stack tests of uncontrolled smouldering fire emissions burning pine needles and, thus, may only represent an approximation of conical burner emission factors.

5. Based on tests at a liquid injection incinerator with scrubber/baghouse emission controls that burn low chlorinated and non-PCB containing wates.

6.4 Commercial/Institutional Waste Incineration

6.4.1 Process Description

Commercial waste incinerators are typically small-scale controlled air, packaged, dual or multichamber waste reduction units used in commercial buildings, schools, apartment buildings, hotels, institutions and hospitals. These units usually require firing of an auxillary fuel and emission control devices are generally not used (U.S. EPA 1987a, Environment Canada 1976, MOE 1986). According to an earlier U.S. study (conducted in 1972), approximately 100,000 intermediate-sized incinerators existed in the U.S. and were primarily multiple-chamber units with an average capacity of 102 kg refuse charged per hour (range 20-2000 kg/hr) (Energy and Environmental Analysis 1978). Commercial incinerators were noted to typically operate an average of 3 hours per day for 260 operating days per year. Such incinerators may be characterized by inefficient combustion with a tendency to emit PAH and other products of incomplete combustion. However, the actual extent of commercial/institutional incineration (i.e. base quantities) is extremely uncertain. Because of the high plastics content of hospital and biomedical wastes in comparison with municipal wastes, greater potential may exist for emissions of HCl and other chlorinated constituents such as PCDDs and PCDFs (Powell 1987, Doyle et al 1985). For example, hospital wastes are reported to contain 20% plastics, comprising PVC and other halogenated polymers, compared with 3 to 7% plastics content in municipal wastes (Keating 1986). The detailed characteristics of hospital waste composition also has been documented (Brunner and Brown 1988). Concern has been expressed that hospital incinerator emissions may be locally significant in the U.S. since only ~15% of American hospitals use the more modern controlled air incinerators and the older units may not completely destroy hazardous materials (Doyle et al 1985, Chang and Hickman 1989).

The technology and state regulations for biomedical waste incineration have recently been described with respect to these issues (Brunner and Brown 1988). Several are not equipped with control devices and few specific hospital waste disposal regulations for incineration exist.

6.4.2 Emission Factors

Emission factors for commercial and institutional incinerators are shown in Table 6.4.1. The PCDD and PCDF emission factors for commercial incinerators were based on average factors for modular excess and starved air municipal solid waste incinerators (U.S. EPA 1989), and the PAH factors were averaged from measurements at two uncontrolled single-chamber commercial incinerators (U.S. EPA 1987a). Concentrations of PCDD, PCDF, PCB and PAH have also been reported for several small-scale, batch type incinerators in Norway used in high-rise buildings (Benestad et al 1987, Oehine et al 1987). Although these data indicated the presence of these species in emissions, insufficient data were available to determine emission factors based on throughputs for comparison with the above factors.

Average dioxin and furan emission factors for one Canadian hospital (Environment Canada 1983b) and two U.S. hospitals (Radian 1987) are shown in Table 6.4.1. Generally, favourable agreement was found between measurements at those units. Results at one of the hospitals also indicated that only a slight reduction of these components occurred with the use of a fabric filter emission control device (Radian 1987, Chang and Hickman 1989). It is evident that the emission factors for biomedical waste incineration are somewhat greater than some other types of incinerators such as the more recent MSW designs and other small-scale units but less than those of older MSW incinerators. It should be noted that the higher chlorinated dioxin and furan homologs were prevalent in these emission measurements but it is uncertain whether or

not vapour phase components were collected during testing. The emission factor for total PCBs was based on measurements only at the Canadian hospital (Environment Canada 1983b).

6.4.3 Inventory Comments

The commercial solid waste emission factors were applied to base quantities for point and area sources contained in the NAPAP files in accordance with the SCC's for commercial/institutional general solid waste incineration and apartment incinerators. Similarly, the hospital waste incineration emission factors were applied to SCC's associated with government and special incinerators burning pathological wastes. Because the number of incinerator facilities that might exist in commercial or institutional establishments in essentially unknown, base quantities for this sector are extremely uncertain. Per capita waste generation data have been reported for general activities (Environment Canada 1976, U.S. EPA 1981c) and for hospitals in kg/bed/day (Powell 1987, MOE 1986, Brunner and Brown 1988). However, the relative amounts of these wastes being either incinerated or landfilled are very uncertain. Estimates of commercial refuse base quantities have been done by Environment Canada in a manner similar to the industrial waste sector by using a 9:l6.6 ratio of industrial and commercial waste to municipal wastes that are incinerated (Environment Canada 1986). These wastes are further apportioned to the type of incineration facility with the assumption that 75% of industrial and commercial wastes were burned in multiple chamber incinerators and 25% in controlled air units.

In addition, the total amount of hospital waste incinerated in Canada has not been estimated and the total number of hospital incinerators is not known (Sheffield 1985). Ontario questionnaire data for 1985 indicated that only one of 21 hospitals reported incineration of small amounts of pathological waste. However, it is uncertain whether other hospitals record throughputs and/or utilize incinerators. Hence, only a small contribution by hospitals in Ontario can be expected in the inventory.

Table 6.4.1

Emission Factors for Commercial/Institutional Incineration

Pollutant	Single Chamber Commercial Incinerators[1] (mg/tonne Refuse Burned)	Hosptial Incinerators[2] (mg/tonne Biomedical Waste Burned)
Total PCDD	0.47	2.7
2,3,7,8 T_4CDD	0.002	-
T_4CDD	0.038	0.17
P_5CDD	0.062	0.21
H_6CDD	0.11	0.38
H_7CDD	0.13	0.83
OCDD	0.13	1.1
Total PCDF	0.45	5.8
T_4CDF	0.08	0.63
P_5CDF	0.11	1.1
H_6CDF	0.13	1.5
H_7CDF	0.11	1.5
OCDF	0.02	1.1
Total PCB	2.5	29
Total PAH	2090	
Anthracene	104	
Benzo(a)pyrene	117	
Benzo(e)pyrene	99	
Benzo(ghi)pyrene	198	
Coronene	46	
Dibenzo(def,mno)chrysene	15	
Fluoranthene	485	
Perylene	7	
Phenanthrene	309	
Pyrene	706	

Notes:

1. Average PCDD, PCDF and PCB emission factors for modular excess and starved air municipal solid waste incinerators (U.S. EPA 1989) and average PAH emission factors for single-chamber commercial incinerators (U.S. EPA 1987a).

2. Average PCDD and PCDF emission factors for biomedical waste combustors (Environment Canada 1983b, Radian 1987), PCB emission factor for a Canadian hospital incinerator (Environment Canada 1983b).

6.5.2 Emission Factors

Emission factors for waste oil combustion, shown in Table 6.5.1, are highly uncertain. For instance, reported emission factors for total PCBs and two PAH constituents have been estimated based on the assumption that 1% of such contaminants originally contained in waste oils (i.e. from stock analysis) are emitted during combustion (Versar 1989). That is, for waste oils containing 39 ppm PCB, the estimated emission factor is 390 mg PCB emitted per Klitre of waste oil burned. On the other hand, a preliminary PCB emission factor reported recently by U.S. EPA for waste oil combination is 900,000 mg/Kl or 0.0075 lb/U.S. gal. (U.S. EPA 1987d). The basis for the latter emission factor is unknown. Similarly, a discrepancy exists for PAH emission factors. For example, the emission factors shown are substantially higher than reported total PAH emission factors of 1.3 to 2.2 mg/Kl for burning waste automotive crankcase oil in an air atomizing heater (U.S. EPA 1987a).

Total dioxin and furan emission factors are shown for a small refractory-wall, mass-burn incinerator burning municipal refuse and waste oil (U.S. EPA 1987f). The fraction attributable to waste oil could not readily be deduced. It should be noted that PCDD and PCDF emissions were not detectable in PCB burning tests conducted in one oil-fired rotary cement kiln (Sheffield 1985). These contaminants have been measured in a rotary cement kiln fired with a combination of petroleum coke and industrial liquid waste solvents (Thorndyke 1984, Sheffield 1985). No significant PCDD or PCDF emission rate differences were found when the kiln was using only petroleum coke or the combined coke/waste as a fuel. However, large uncertainties exist with regard to emission rates for all of the above-mentioned contaminants for burning waste oils in conventional boilers. It should also be noted that waste oil combustion has not been addressed in a recent comprehensive assessment of toxic emissions from coal and oil combustion sources (Brooks 1989).

6.5 Waste Oil Incineration/Combustion

6.5.1 Process Description

There is particular concern and uncertainty regarding potential emissions associated with combustion of waste oils in conventional combustion equipment since no specific controls exist on the quality of oils burned.

For example, this practice could represent a significant source of atmospheric PCBs (Sheffield 1985). It has been estimated that 40-50% of waste oil recovered annually in the U.S. is burned (Versar 1984, U.S. EPA 1988b, Versar 1989). Used vehicle crankcase oil recovered from service stations, represents the principal type of waste oil used for fuel along with other types of oils such as: metal working lubricants, animal or vegetable oils and industrial oils including transformer or other heat transfer fluids (U.S. EPA 1988b). Typical waste oil contaminant levels have been characterized and such oils may contain chlorinated solvents, PCB, PAH amongst other constituents (Versar 1984). The used oils may be physically pretreated by reprocessing, re-refining or blending with clean fuel oil before burning. However, high boiling point contaminants such as PCB and PAH are generally not removed by pretreatment and significantly greater emissions of several pollutants can be expected from waste oil combustion than by burning virgin fuel oils. Approximately 2.2 billion litres of waste oil is burned per year in the U.S. (U.S. EPA 1988b) and an estimated 33 million litres is burned in Canada (Sheffield 1985). Most (~77%) is burned in industrial boilers with the balance in commercial, institutional and residential combustion equipment (Versar 1989). In Canada, some of the waste oil is burned as supplementary fuel in cement manufacture and in other industrial and utility applications. In small space heaters, in which there has been increased waste oil usage, the conventional air atomizing burner produces greater emissions than the oil vapourizing burner (U.S. EPA 1988b). No additional emission control devices have been applied to waste oil combustion facilities.

6.5.3 Inventory Comments

The amount and quality of waste oil used in Ontario and the apportionment to fuel combustors has not been estimated and, thus, emission rates have not been determined. For example, the extent of waste oil used in utility, industrial or commercial boilers or cement kilns is not known. However, should a significant fraction of the estimated Canada-wide consumption of waste oil (i.e. 33 million litres) be used in boilers in Ontario, waste oil combustion could represent a major source of PCB emissions, especially if low concentration transformer oils are blended with used lubricating oils. Similarly, the limited amount of waste oil base quantity information available for the U.S. does not permit a reasonable estimate of emission rates to be made. Hence, further information is required on the quantities, quality (e.g., PCB content) and facilities in which waste oil is burned in order to estimate emissions associated with use of this fuel. In addition, it would be necessary to separate waste oil fuel consumption from conventional oils used for given sources reporting oil combustion so as to avoid double counting of emissions.

Table 6.5.1

Emission Factors for Waste Oil Incineration/Combustion

Contaminant	Emission Factor (mg/tonne Waste Oil Burned)
Total PCB[1]	390
Benz(a)anthracene[1]	160
Benzo(a)pyrene[1]	100
Total PCDD[2]	0.0452
Total PCDF[2]	0.320

Notes:

1. Estimated emission factors for waste oil combustion assuming a fraction (i.e. 1%) of contaminants in waste oil are emitted (Versar 1989)

2. Emission factors based on measurements at a small refractory, mass-burn incinerator (Mayport Naval Station Facility) burning waste oil and municipal refuse (U.S. EPA 1987f).

In addition, homologues of dioxins and furans have recently been measured in test car exhausts when using leaded gasoline (i.e. without catalysts) (Marklund et al 1987). Results inferred that these contaminants may have originated from chlorine-containing fuel additives (e.g. dichloroethane scavengers in leaded fuels) rather than oil additives. Because these components were not detected in exhaust of unleaded test vehicles (i.e. fueled without additives), it was deduced by the investigators that these contaminants either did not form or that they were removed by the catalysts. Although such compounds have been detected in scrapings of automotive exhaust systems (Sheffield 1985), the Swedish data noted above appear to be the only measurements of exhaust-related emissions that have been found.

Speciated emission factors associated with various gasoline-powered vehicles, as derived from several publications are shown in Tables 7.1.1, 7.1.2 and 7.1.3. Only some of these are based upon direct measurements and expressed in units of component mass per vehicle kilometre travelled (VkmT). Emission factors reported in terms of fuel usage were converted to a VkmT basis using 1985 fleet specific fuel economies derived from MOBILE 3 (U.S. EPA 1985) as follows:

LDGV	-	29.8 km/U.S. gal.
LDGT1	-	24.2 km/U.S. gal.
LDGT2	-	16.8 km/U.S. gal.
HDGV	-	13.3 km/U.S. gal.

Many of the PAH emission factors were derived by a U.S. committee for specific vehicle classes for which no data were available (U.S. EPA 1987a). Catalytic controlled emissions (especially 3-way catalysts) were reported to be lower than emissions from non-catalyst vehicles for most PAH compounds. Total PCDD emission factors of 640 and 2,240 pg/km have been estimated by EPA for catalyst-equipped and leaded gasoline cars

respectively (Sheffield 1985). Speciated emissions, however, reported by Marlund et al (1987) were used in this inventory.

7.1.3 Inventory Comments

Based on the literature review discussed in Section 7.1.2, four PAH emission factor files, in mg/VkmT, were derived for gasoline powered motor vehicles:

LDV	-	leaded
LDV	-	unleaded (3-way catalyst)
LDV	-	unleaded (oxidation catalyst)
HDGV	-	leaded, non-catalyst

Two PCDD and PCDF emission factor files, in mg/VkmT were derived:

LDV	-	leaded
LDV	-	unleaded (all catalyst)

The LDV-leaded emission factor file for PCDD and PCDF LDV-leaded was applied to HDGV in absence of more source specific data.

Base quantity data for Ontario, available in VkmT, were grouped as follows:

Passenger	}	
Taxis	}	
Light Duty Trucks	}	Light Duty Vehicles
Medium Duty Trucks	}	
Heavy Duty Trucks	}	Heavy Duty Gas Vehicles
Buses	}	

Line sources (major freeway and other highways) were assumed to be 91.5% LDV, 2.5% HDGV and the remainder diesel (Ontario Research Foundation 1983). These data are available on the MOE UTM grid.

7. MOBILE TRANSPORTATION

7.1 Gasoline Powered Motor Vehicles

7.1.1 Sector Description

7.1.1.1 Light Duty Gasoline Powered Vehicles

Light duty gasoline powered vehicles (LDGV) are responsible for a large portion of criteria air pollutant emissions in many areas of Canada and the United States. A LDGV is usually defined as any gasoline fueled automobile designated primarily for transportation of persons and having a capacity of 12 persons or fewer. Two other light duty gasoline vehicle categories are inventoried: light duty gas trucks I (LDGT1) and light duty gas trucks II (LDGT2). LDGT1 have a gross vehicle weight (GVW) of 6000 pounds or less and are typically used for personal transportation and light hauling. LDGT2 have a GVW between 6001 and 8500 pounds (U.S. EPA 1985).

In this report, all of these classes (LDGV, LDGT1 and LDGT1) are grouped together as light duty gas vehicles (LDV).

7.1.1.2 Heavy Duty Gasoline Powered Vehicles

A heavy duty gasoline powered vehicle (HDGV) is defined to be any gasoline fueled motor vehicle designated primarily for the transportation of property and rated at more than 8500 pounds GVW, or designated primarily for transportation of persons and having a capacity of more than 12 persons (U.S. EPA 1985).

7.1.1.3 Other Gasoline Powered Highway Mobile Sources

Motorcycles were not inventoried due to a very limited data base.

7.1.2 Emission Factors

Internal combustion engine exhaust contains vapour and particulate organic materials as products of incomplete combustion of fuels, additives and lubricants burned. The primary operational and fuel factors that influence such emissions are (U.S. EPA 1987a, Bjorseth and Ramdahl 1985):

- air-to-fuel ratio (e.g. extent of fuel richness or choking)
- presence and maintenance of emission controls
- vehicle age or extent of deterioration (e.g. oil consumption, combustion chamber deposits)
- mode of operation (e.g. cold operation, acceleration, etc.)
- fuel type (aromaticity, contaminant content)
- presence and extent of combustion of fuel additives or lubricants

Despite some conflicting evidence on the emission effects of these factors, data suggest that the presence of catalysts and extent of vehicle deterioration are of major significance in the rate of PAH emissions from gasoline engines. For example, unlike diesel engines, it is conceivable that the vacuum created in combustion chambers may draw in crankcase oil that is known to accumulate PAH components to cause an increase of emissions, especially when cylinders are worn (U.S. EPA 1987a, Stenberg et al 1983). However, not all data consistently support this (Bjorseth and Ramdahl 1985). Furthermore, it is generally accepted that nitro-PAH compounds are formed after combustion due to reactions between particulate PAH and nitrogen oxides in the exhaust (U.S. EPA 1987a). This is not without question due to uncertainties in measurement techniques (e.g., nitro-PAH sampling artifacts) (Fellin et al 1985).

Base quantities for the remainder of Canada were derived from NAPAP emissions using vehicle class specific emission factors (Versar Inc. 1989) grouped as follows:

LDGV-Auto LDGV-Trucks	} }	Light Duty Vehicles
HDGV		

Data were available on a provincial basis. Population was used as a spatial allocation surrogate, using files from Conservation and Protection, Environment Canada created for the 1985 NAPAP inventory.

Base quantities for the U.S. were available as total fuel (U.S. gals.) for LDV and HDGV on a county basis (the 1985 NAPAP Emissions Inventory (Version 2) Annual Emissions "County" File). The LDV was split into leaded (35.5%) and unleaded (64.5%) (U.S. DOE 1985). All classes were then converted into VkmT using fuel economies presented in Section 7.1.2. Data was spacially allocated using the country centroid file.

Once LDV base quantities were available in VkmT, these had to be split into the subcategories mentioned above for all of the MOE, Canadian and U.S. data. The following 1985 LDGV fleet specific travel weighting fractions were used as appropriate to split the above data into the required LDV groupings (U.S. EPA 1985):

Class	Travel Fraction
leaded	.172
unleaded (3-way)	.465
unleaded (oxidation)	.364

Temporal factors were taken from the appropriate U.S. area code temporal factor files.

All LDV emissions were assigned to Master Sector Code 40101. All HDGV emissions were assigned to Master Sector Code 40201.

TABLE 7.1.1

PAH Emission Factors for Light Duty Gasoline Vehicles (mg/VkmT)

Compound	Unleaded Gasoline		Leaded Gasoline
	Oxidation Catalyst	3-Way Catalyst	
Anthracene	$7.4x10^{-3}(2.5x10^{-5} - 1.4x10^{-2})$ abg	$1.6x10^{-3}$ g	$2.5x10^{-2}(7x10^{-4} - 7.5x10^{-2})$ agl
Benz(a)anthracene	$3.7x10^{-3}(8x10^{-5} - 8.5x10^{-3})$ bcg	$2x10^{-4}$ g	$1.6x10^{-2}(5.8x10^{-3} - 5.0x10^{-2})$ acdglmn
Benzofluoranthenes	$9.2x10^{-3}(4x10^{-4} - 2.3x10^{-2})$ adg	$5.0x10^{-4}$ g	$1.5x10^{-2}(6.5x10^{-3} - 2.3x10^{-2})$ gl
Benzo(a)fluorene	$4.6x10^{-3}$ g	$5.4x10^{-4}$ g	$2.5x10^{-2}$ g
Benzo(ghi)perylene	$6.1x10^{-3}(7x10^{-4} - 9.5x10^{-3})$ bcdg	$5.4x10^{-4}$ g	$1.4x10^{-2}(4x10^{-3} - 2.6x10^{-2})$ cdgl
Benzo(a)pyrene	$1.4x10^{-3}(4.4x10^{-5} - 4.5x10^{-3})$ acdfghij	$1.8x10^{-3}(2x10^{-4} - 2.7x10^{-3})$ fg	$5.6x10^{-3}(5.9x10^{-4} - 2.3x10^{-2})$ acdefghijlmnopq
Benzo(e)pyrene	$7.4x10^{-3}(2.6x10^{-4} - 2.0x10^{-3})$ abg	$2x10^{-4}$ g	$6.0x10^{-3}(1.7x10^{-3} - 1.1x10^{-2})$ agln
Chrysene	$3.0x10^{-3}(2x10^{-4} - 5.8x10^{-3})$ dg	6.7×10^{-4} g	$1.6x10^{-2}(6.9x10^{-3} - 3.2x10^{-2})$ dgl
Coronene	$3.6x10^{-3}(1.7x10^{-4} - 1.0x10^{-2})$ abcdg	3.7×10^{-4} g	$6.3x10^{-3}(2.6x10^{-4} - 1.7x10^{-2})$ acdglnoq
Cyclopenta(cd)pyrene	$1.5x10^{-2}(6x10^{-5} - 3.1x10^{-2})$ bdg	$1.8x10^{-3}$ g	$3.2x10^{-2}(4.5x10^{-3} - 8.3x10^{-2})$ dgl
Dibenz(ah)anthracene	$4.7x10^{-4}$ g	$7x10^{-5}$ g	$2.7x10^{-3}$ g
Fluoranthene	$1.5x10^{-2}(7x10^{-5} - 3.1x10^{-2})$ abdg	$3.5x10^{-3}$ g	$4.8x10^{-2}(1.4x10^{-3} - 1.6x10^{-1})$ adgl
Indeno(1,2,3-cd)pyrene		$1.3x10^{-3}(3x10^{-4} - 2.3x10^{-3})$ bdg	1×10^{4} g $3.5x10^{-3}(1.3x10^{-3} - 6.4x10^{-3})$ dgl
Methylphenanthrenes	$3.5x10^{-2}$ g	$4.1x10^{-3}$ g	$1.9x10^{-1}$ g
1-nitropyrene	$1.4x10^{-4}(2.9x10^{-5} - 3.4x10^{-4})$ gijk	1×10^{-5} g	$1.3x10^{-4}(1x10^{-4} - 1.8x10^{-4})$ egij
Perylene	$4.2x10^{-4}(1.7x10^{-4} - 2.5x10^{-4})$ ag	$3x10^{-5}$ g	$5.9x10^{-4}(4x10^{-4} - 9.1x10^{-4})$ agl
Phenanthrene	$2.0x10^{-2}(6x10^{-5} - 6.6x10^{-2})$ abdg	$6.6x10^{-3}$ g	$6.4x10^{-2}(1.2x10^{-3} - 3.1x10^{-1})$ adglo
Pyrene	$1.1x10^{-2}(2x10^{-4} - 3.7x10^{-2})$ abdegij	$4.4x10^{-3}$ g	$1.1x10^{-1}(1.8x10^{-3} - 7.6x10^{-1})$ adegijlnoq

TABLE 7.1.1 (contd.)

PAH Emission Factors for Light Duty Gasoline Vehicles (mg/VkmT)

Notes

a McKee et al 1979. This data, as cited by Carhart and Walsh (1987) is for PROCO engines with and without oxidation catalyst. It is not specified whether these results are for particulate or total emissions.

b Westerholm et al 1988. Test results are for a 1984 Volvo 240 (manual gearbox) driven according to the U.S. Federal Test Procedure (FTP-73). Results are for the total of gaseous and particulate emissions. Generally the gas phase was found to contribute more to total PAH emissions.

c Stenberg 1979. Tests were performed on 34 vehicles in different driving cycles, both cold and hot start. PAH's were determined for both particulates and gas phase.

d Egebäck 1982. Data from an investigation on the PAH emission from different vehicles and fuel combinations. The samples were taken in a dilution tunnel and represent the particulates phase. Emissions are from FTP, cold start.

e Williams and Swarin 1981. Data represent only particulate as sampled in a dilution tunnel. Mixture of cold and hot start, FTP.

f Victorin et al 1988. Eight vehicles using various fuels and control systems were tested using US-73 and ECE-15 test procedures. Results are for the particulate phase only.

g Committee on Pyrene and Selected Analogues 1983. Measured emission factors for noncatalytic leaded gasoline vehicles. All others are derived. Not specified as to whether these represent total (i.e., gaseous or particulate) emissions. The derived emission factors have an uncertainty of a factor of two or more and are generally over estimates compared to values in the literature.

h Gross 1970. Gasoline automobiles of model year 1966-1976 were tested. Particulate emissions were sampled by filtration during cold-start cycles.

TABLE 7.1.1 (contd.)

PAH Emission Factors for Light Duty Gasoline Vehicles (mg/VkmT)

Notes

i Lang et al 1981. A fleet of 20 light-duty gasoline passenger cars and trucks were tested under various test cycles (cold start FTP, hot start HWFET as well as hot start FTP (LA-4), COE and NYCC cycles). Results are for particulate emissions only.

j Gibson 1982. Data represent particulate PAH collected in a dilution tunnel during the 23-minute Hot Start Phase of the FTP.

k Tejada et al 1982. Data represent particulate PAH collected in a distribution tunnel on 6 light-duty vehicles under a variety of driving cycles (FTP, LA4, HWFET, S-7, NYCC).

l Alsberg et al 1985. A Saab 900 GL (noncatalyst, leaded gasoline) was tested. Particulate samples were collected in a dilution tunnel. Test cycle was a cold-start US-73. In all, 36 samples were collected by using two series done at different times.

m Gross 1972. Particulate emission rates are reported for 3 vehicles and focused on the impact of PAH contents of the fuel and emissions control on PAH emissions.

n Kraft and Lees 1981. Data represent both gas and particulate phase PAH from a 1975 FTP and VW vehicles.

o Hangebrauck et al 1966. A mobile sampling system was used on two vehicles driven on a "realistic composite of business arterial and rapid transit driving". Likely represents particulate emissions.

p Handa et al 1979. Tests performed in Japanese 10-mode driving cycle which simulates city driving. Includes cold and hot start. Not specified if total PAH.

q Fiat 1980. Data from small engines in vehicles driven in the ECE test cold start. Not specified if total or particulate PAH.

TABLE 7.1.2

PCDD and PCDF Emission Data for Light Duty Gasoline-Fuelled Cars (mg/VkmT)*

	Mid-Range	Range
Leaded Gasoline (n=4)		
T_4CDD-2,3,7,8	6×10^{-9}	$<2.0 \times 10^{-9}$ - 1.2×10^{-8}
T_4CDD	1.9×10^{-6}	1.2×10^{-7} - 3.6×10^{-6}
P_5CDD	2.1×10^{-6}	2.4×10^{-7} - 4.0×10^{-6}
T_4CDF-2,3,7,8	2.7×10^{-7}	2.4×10^{-8} - 5.2×10^{-7}
T_4CDF	4.3×10^{-6}	4.0×10^{-7} - 8.1×10^{-6}
P_5CDF	1.1×10^{-6}	2.0×10^{-7} - 1.9×10^{-6}
Non-leaded Gasoline (n=2)		
T_4CDD-2,3,7,8	$<2.0 \times 10^{-9}$	
T_4CDF-2,3,7,8	$<8.0 \times 10^{-9}$	

* Marklund et al 1987. Represents total of gaseous and particulate emissions. Detailed data was not available, so the mid-range was chosen to characterize the data.

TABLE 7.1.3

PAH Emission Factors for Heavy Duty Gasoline Vehicles (mg/VkmT)

	Heavy Duty Gasoline Non-Catalyst, Leaded Fuel[a]	Notes
Anthracene	.17	
Benz(a)anthracene	.017	
Benzofluoranthenes	.050	
Benzofluorenes	.056	Assume all Benzo(a)fluorene
Benzoperylenes	.054	Assume all Benzo(ghi)perylene
Benzo(a)pyrene	.021	
Benzo(e)pyrene	.024	
Chrysene	.071	
Coronene	.038	
Cyclopentapyrene	.19	Assume all Cyclopenta(cd)pyrene
Dibenzoanthracenes	.0059	Assume all Dibenz(ah)anthracene
Fluoranthene	.36	
Indenopyrene	.014	Assume all Indeno(1,2,3-cd)pyrene
Methylphenanthrene	.43	
1-Nitropyrene	.0030	
Perylene	.0020	
Phenanthrene	.68	
Pyrene	.45	
Triphenylene	.014	

a All data is from Committee on Pyrene and Selected Analogues 1983. These emission factors are derived. They have an uncertainty of a factor of two or more and are generally overestimates compared to values reported in the literature. Conversions from µg/gal to mg/VkmT were done using a fuel economy of over 13.3 km/U.S. gal. This factor is derived from AP-42 (U.S. EPA 1985) using model year on-road fuel economies combined with model year travel fractions for the 1985 heavy duty gasoline fleet mix.

7.2 Diesel Powered Motor Vehicles

7.2.1 Sector Description

7.2.1.1 Light Duty Diesel Powered Vehicles

A light duty diesel powered vehicle (LDDV) is defined to be any diesel fueled automobile designated primarily for transportation of persons and having a capacity of 12 persons or fewer. A light duty diesel powered truck (LDDT) is designed primarily for transportation of property and rated at 8500 pounds gross vehicle weight or less (U.S. EPA 1985). These categories were not inventoried as they represent a very small percentage of light duty vehicles and data was not available for the U.S..

7.2.1.2 Heavy Duty Diesel Powered Vehicles

A heavy duty diesel powered vehicle (HDDV) is defined as any diesel fueled motor vehicle designated primarily for the transportation of property and rated at more than 8500 pounds of gross vehicle weight.

7.2.2 Emission Factors

Diesel engines are known to be a source of PAH emissions especially under conditions of overloading and poor engine maintenance (U.S. EPA 1987a). It has been reported that diesel automobiles emit significantly more particulate matter and PAH than gasoline engines equipped with catalytic converters. This is thought to be due, in part, to the lower combustion chamber temperatures of diesel engines (U.S. EPA 1987a). Neither engine crankcase oil nor fuel PAH content, which is reported to be lower than gasoline, were found to significantly affect PAH emission rates from diesel engines. Emission factors, derived by a U.S. committee, indicated higher diesel vehicle emission factors of all PAH constituents than for leaded and

non-leaded gasoline vehicles (U.S. EPA 1987a). However, tunnel test data conducted in Japan that compared gasoline and diesel emission factors for 50 mi/hr speeds indicated higher nitro-PAH factors for diesel engines but lower factors for several other parent PAH constituents (U.S. EPA 1987a). Similarly, EPA comparative tests under FTP test cycle conditions, showed significantly higher pyrene and 1-Nitropyrene emission factors by conventional diesel automobiles than gasoline automobiles but substantially lower benzo(a)pyrene and 6-Nitro-benzo(a)pyrene in diesel emissions (U.S. EPA 1987a). Hence, there appears to be major uncertainties regarding the relative PAH contributions between gasoline and diesel engines, perhaps due to the limited measurement data that are available.

Emission factors of PAH for heavy duty diesel engines shown in Table 7.2.1 represent particulate emissions only. No dioxins were found in one set of diesel samples analyzed by EPA (the sample medium was not indicated in the reference) but dioxins were found in one of two muffler-scraped samples from diesel-burning trucks (Sheffield 1985).

7.2.3 Inventory Comments

Based on the review discussed in Section 7.2.2, one PAH emission factor file, in mg/VkmT, was derived for heavy duty diesel powered vehicles. Neither PCDD nor PCDF emissions were estimated.

For Ontario, the HDDV base quantity was derived by adding heavy duty trucks, buses and 3% of line sources (Ontario Research Foundation 1983), all of which were available in VkmT. Data was available on the MOE UTM grid.

Base quantities for the remainder of Canada were derived for HDDV from NAPAP emission data using 1985 vehicle class specific emission factors based on Carey (1987). Data were available on a provincial basis.

Population was used as a spacial allocation surrogate, using files from Conservation and Protection, Environment Canada, created for the 1985 NAPAP inventory.

Base quantities for the U.S. were available as total fuel (U.S. gals.) for HDDV on a county basis (the 1985 NAPAP Emissions Inventory (Version 2) Annual Emissions "County" File). This was converted into VkmT using a fuel economy of 9.8 km/U.S. gal. (Kelly 1983). Data was spacially allocated using the county centroid file.

Temporal factors were taken from the appropriate U.S. area code temporal factor files.

All HDDV emissions were assigned to Master Sector Code 40401.

TABLE 7.2.1

PAH Emission Factors (Particulate Only) for Heavy Duty Diesel Vehicles (mg/VkmT)

Compound	Emission Factors Average	Range
Anthracene	.14 ab	(.003 - .27)
Benz(a)anthracene	.021 abcd	(.00057 - .23)
Benzofluoranthenes	.047 ab	(.006 - .087)
Benzo(b)fluoranthene	.015 cde	(ND .19)
Benzo(k)fluoranthene	.0072 cde	(ND - .088)
Benzofluorene	.091 a	
Benzo(ghi)perylene	.039 abde	(ND - .4)
Benzo(a)pyrene	.016 abcde	(ND - .19)
Benzo(e)pyrene	.017 abe	(ND - .048)
Chrysene	.068 ab	(.025 - .11)
Coronene	.031 ab	(.0007 - .061)
Cyclopenta(cd)pyrene	.0039 b	
Dibenz(ah)anthracene	.0067 ad	(.0037 - .0096)
Fluoranthene	.060 bcde	(.018 - .33)
Indeno(1,2,3-cd)pyrene	.019 abd	(.0023 - .031)
Methylphenanthrenes	.69 a	
1-nitropyrene	.011 adfg	(.00025) - .013)
Perylene	.0043 ae	(ND - .0073)
Phenanthrene	.56 ab	(.025 - 1.1)
Pyrene	.31 abe	(.035 - .73)
Triphenylene	.023 a	

a Committee on Pyrene and Selected Analogues 1983. Emission factors were derived for diesel engines, non-catalyst. Data have an uncertainty factor of two or more and were considered to be overestimates. Conversions from µg/gal to mg/VkmT were done using a fuel economy of 9.8 km/U.S. gal (Kelly 1983). Data was only used if it was in the range of other studies or the only data available. It was not reported if these were for total or particulate emissions.

TABLE 7.2.1 (Cont'd)

b Westerholm et al 1986. Three emission tests were run on a truck equipped with a turbo-charged Scania DS11 15 diesel engine. Tests were done for a bus cycle. The vehicle was operated on a chassis dynamometer. Results used were for no trap, .26% sulphur diesel fuel. Particulates only.

c Wall and Hoekman 1984. Fifteen emissions tests were run on a Cummins NTC Test Engine (turbocharged direct injection diesel). This engine represents over 90% of Cummins engine production and 45-60% of all heavy-duty diesel engines in haul-line service in the U.S. The engine was run at three steady-state operating conditions (idle, cruise and highpower) over a six-step test procedure. A commercial diesel fuel was used. Particulates only. Results were converted to mg/VkmT based on 1985 HDD fleet-specific particulate emission rates (class 7-8) based on Carey 1987.

d Hoekman and Ingham 1987. The same engine as in c above was used. The test sequence consisted of eight engine conditions, under each of which three one-hour particulate samples were collected. The fuel was a commercial No.2 diesel fuel produced by Chevron. Results were converted to mg/VkmT based on 9.8 km/U.S. gal (Kelly 1983).

e Zierock et al 1983. The engine tested was a 4 cylinder direct injection diesel engine used in trucks of the 6-8 ton category. The diesel fuel was high sulphur (.31%). The engine was mounted on a dynamomter and operated in 20 steady-state modes at various loads and revolutions to cover the whole range of performance characteristics. Particulates only. Results were converted to mg/VkmT based on 1985 HDD fleet-specific particulate emission rates (Classes 2B, 3-5 and 6) based on Carey 1987.

f Draper 1986. Diesel particulates collected from a Caterpillar 3304 naturally-aspirated heavy-duty diesel engine coupled to a dynamometer in a test cell. This engine is approved for use in mining. Particulate concentrations were converted as for Wall and Hoekman 1984 (see c above).

g Schuetzle and Perez 1983. Particulates from a 4-stroke (assumed to be class 7-8) were analysed. Conversions were done as for Wall and Hoekan 1984 (see c above).

7.3 Marine

7.3.1 Sector Description

Vessels may be classified on the basis of use into two general categories: commercial/military and pleasure craft. These categories vary both in vessel size and usage characteristics.

Recreational boats are generally less than 100 feet in length, most being less than 30 feet. Those with outboard engines are gasoline powered and usually are designed to operate on a 2-stroke cycle. Inboard engines may be either gasoline or diesel powered and tend to resemble automobile engines in terms of design, size and performance (U.S. EPA 1981b).

Commercial vessel sizes range from 20-foot charter boats to the largest tankers and military vessels. The majority of vessels in this category are powered by diesel engines or steam turbines. These are commonly called motorships (diesel) and steamships. The predominant fuel for both types is oil, both distillate and residual grades. Steamships and very large diesel engines are fueled with the heavier oils, while lighter diesel engines require distillate oil, although some residual may be added (U.S. EPA 1981b).

Further details on both of these classes may be found in U.S. EPA 1981b and 1985.

7.3.2 Emission Factors

Emissions from marine vessels are generated during dockside activities and during shipping. Emissions from dockside activity include the fuel consumption associated with entering and leaving port, docking, maneuvering and power generation. PAH emissions can be expected from

these activities due to the fuel types used in these vessels. A review of the literature, however, did not identify any reports on such emissions.

In order to provide a preliminary estimate of the contribution of these sources to PAH emissions in general, "surrogate" emission factors were chosen. External combustion industrial residual-oil fired boilers were selected as being similar to residual oil-fired steamships. PAH emissions from diesel-fueled reciprocating internal combustion engines were used to represent emissions for motorships. For recreational boats, PAH emission factors were derived using reported factors for gasoline-powered vehicles as a surrogate.

7.3.3 Inventory Comments

A review of the available base quantity data showed that Ontario and U.S. data was available in terms of fuel usage. Canadian data for the other provinces was available in terms of vessel type, with commercial vessels being further divided into dockside (number of calls in port) and underway (fuel usage).

The surrogate emission factors chosen in the previous section (7.3.2) are on the basis of mg/kl for all vessels. Therefore, Canadian data for numbers of calls in port (steamships and motorships) and Kwh (gasoline outboard) could not be readily used. Since the total potential for emissions for these categories was not large, it was decided to be inappropriate to expend further resources on developing these base quantities into a usuable form and they were dropped. In addition, a simplifying assumption was made for U.S. and Ontario data for fuel usage. It was assumed that all residual oil is burned in steamships and all distillate (diesel) oil is burned in motorships. All gasoline was assumed to be used in recreational vessels.

The final marine inventory may be summarized as follows:

Source	Ontario	Other Canada	U.S.
residual oil	steamship all	steamship underway	steamship all
diesel	motorship all	motorship underway	motorship all
gasoline	not inventoried	not inventoried	all

Temporal factors were taken from the appropriate U.S. area source NAPAP files. MOE data was available on the UTM grid. U.S. data was by county. Canadian data for other provinces was available by province and was geographically allocated by population.

Emissions were assigned to the appropriate Master Sector Codes as follows:

40802	-	Vessel	-	Diesel Oil
40803	-	Vessel	-	Residual Oil
40804	-	Vessel	-	Gasoline

7.4 Aircraft

7.4.1 Sector Description

Aircraft may be categorized by aircraft type (jet, turboprop, piston and helicopter) or by the sector using the aircraft (military, civil and commercial). The former method is used in Ontario and Canadian inventories, the latter in U.S. inventories.

Whatever the inventory method, it is necessary to develop emission factors for many types of aircraft. Aircraft emissions are affected by the throttle power setting, which is fairly predictable based on the specific operating mode in which the aircraft is operating. Two broad categories of aircraft emissions may be considered: the landing/takeoff cycle (LTO) and inflight emissions (U.S. EPA 1981b).

The LTO cycle consists of the following operating modes (U.S. EPA 1981b):

approach
taxi/idle in
taxi/idle out
takeoff and
climb out

Traditionally, only LTO cycles are inventoried. These emissions occur between ground level and the above ground inversion height and so affect air quality at ground level.

7.4.2 Emission Factors

No emission factors were found in the literature reviewed. Some limited data is available on PAH concentrations in exhaust particulate from small

aircraft gas turbine engine burning conventional fuel (Robertson 1979). Following Longley (1989), this was developed into a single LTO based emission factor which was applied to all LTO cycles (see Table 7.4.1). Although this method was extremely simplified in comparison to inventories of criteria pollutants and although more detailed data has subsequently been published (Spicer et al 1988), it was felt that the total potential for this sector did not warrant further dedication of resources during this preliminary inventory.

7.4.3 Inventory Comments

In Section 7.4.1, it was noted that Ontario and Canadian aircraft activity levels are available in terms of aircraft type and U.S. aircraft activity levels are available in terms of sector use. This did not cause difficulty in the preliminary inventory, however, as all were available as LTO cycles and only a single emission factor was developed at this time.

Ontario data was available on the UTM grid and Canadian data was available by province. Population was used as a surrogate for spatial allocation of this data. U.S. data was available on a county basis.

Temporal factors were available for each of the U.S. area codes (military, civil and commercial). An average of the Michigan temporal factors for these three codes were used for the Ontario and Canadian aircraft emissions.

All emissions were assigned to a single Master Sector Code: 4060l.

Table 7.4.1

**PAH Particulate Emission Factors
For Aircraft (mg/LTO)**

Compound	Emission Factor
Anthracene	3.62
Benz(a)anthracene	.65
Benzo(a)pyrene	1.24
Benzo(e)pyrene	.36
Benzo(ghi)perylene	1.62
Chrysene	3.08
Fluoranthene	37.1
Phenanthrene	47.8
Pyrene	43.2

Notes:

Based on Longley (1989). Since emission factor data were not available, the emissions were estimated based on data from several sources. The average exhaust rate of a Jumbo 747 airplane was stated to be 158m^3/s (Sep 1989). PAH emission concentrations from Robertson (1979) were used for all airplanes in the absence of better data. The resulting emission rates were then multiplied by a 32.9 minute LTO cycle duration for a commercial jumbo jet (U.S. EPA 1985).

7.5 Locomotives

7.5.1 Sector Description

Diesel-electric locomotives use a diesel engine and generator to produce the electricity necessary to power their electric traction motors. While other types of locomotives are in use (i.e. steam, diesel-hydraulic, gas-turbine) their numbers are insignificant compared to diesel-electric locomotives (U.S. EPA 1981b).

7.5.2 Emission Factor

No emission data or emission factors for locomotives were found in the literature for any of the compounds of interest to this inventory. The diesel-fueled reciprocating internal combustion PAH emission factors (based on fuel usage) discussed in Section 5.7 were used to represent emissions from this sector.

7.5.3 Inventory Comments

Activity level data for all areas was available on a diesel fuel usage basis (kl), although data from NAPAP (Canada (other) and U.S.) had to be derived from TSP emissions using emission factors from the U.S. file.

Ontario data was available on the UTM grid. Canada (other) data was by province was spatially allocated using population as a surrogate. U.S. data was available on a county basis and was allocated using a county centroid file.

Canada (other) and Ontario temporal files were taken from the Michigan temporal factor file.

All emissions were assigned to Master Sector Code 40701.

7.6 Off-Highway Use of Gasoline

7.6.1 Sector Description

This sector includes all off-highway gasoline consumption and covers a wide range of equipment:

- agricultural
- construction
- industrial
- motorcycles
- snowmobiles
- lawn and garden equipment

Details on what each of these categories represent can be found in U.S. EPA (1985) and U.S. EPA (1981b).

7.6.2 Emission Factors

Very limited emission data was found for any of the above categories. Since activity data representing primarily the heavier equipment classes listed above was available on the basis of total fuel usage (see Section 7.6.3), the heavy duty gasoline vehicle PAH emission factors (Section 7.1) were considered to be suitable surrogates for this sector. No attempt was made to estimate PAH emissions from snowmobiles, lawn and garden equipment or motorcycles.

7.6.3 Inventory Comments

Total off-highway gasoline fuel use data for Ontario was available in kl on the MOE grid.

For Canada (other) general off-highway gasoline use (excluding snowmobiles), was derived using NAPAP TSP emission factors and total TSP emissions by province. Industrial population was used to spacially allocate these emissions.

For the U.S., total off-highway gasoline use was also derived from NAPAP TSP emission factors and TSP emissions by county. Spacial allocation was completed using the county centroid file.

Temporal factors for all regions were taken from the NAPAP U.S. area source temporal factor file for SCC 039 (off-highway gasoline).

Emissions were assigned to Master Sector Code 40301.

7.7 Other Diesel Engines

7.7.1 Sector Description

This sector, which covers all off-highway use of diesel-fuel powered equipment, includes all or some of the following (depending on the area being inventoried):

- agricultural
- construction
  industrial (manufacturing included)
- mining
- forestry
- public administration
- pipeline

Details on these categories can be found in U.S. EPA (1985) and U.S. EPA (1981b).

7.7.2 Emission Factors

The only off-highway diesel equipment PAH emission study identified in the literature review was a study of PAH air concentrations in underground mines (Mogan et al 1983). This information was collected as part of a occupational health risk assessment program. Insufficient data was available with which to derive an emission factor. The heavy duty diesel PAH emission factors discussed in Section 7.2 were used as surrogates for this sector, since the majority of fuel usage by this sector is by heavy equipment (U.S. EPA 1981b).

7.7.3 Inventory Comments

Total off-highway gasoline fuel use data for Ontario was available in kl on the MOE grid.

For Canada (other), the off-highway diesel fuel use by agricultural, construction, mining, manufacturing, forestry, public administration and pipeline equipment was derived using NAPAP TSP emission factors and total TSP emissions by province. The emissions were spatially allocated using the following surrogates:

- agricultural - agricultural labour force
- construction - population
- mining - mining labour force
- manufacturing - commercial labour force
- forestry - mining labour force
- public administration - population
- pipeline - mining labour force

For the U.S., total off-highway gasoline use was derived from NAPAP TSP emission factors and TSP emissions by county. Spatial allocation was completed using the county centroid file.

Temporal factors for all areas were taken from the NAPAP U.S. area source temporal factor file for SCC 044 (off-highway diesel).

Emissions were assigned to Master Sector Code 40501.

8. OPEN SOURCE EMISSIONS

8.1 Overview of Toxic Emissions from Open Water and Soil Sources

Emissions from open water and soil sources may be of primary nature in that they result from toxic spills or deliberate application of toxic chemicals to water, soil and/or vegetation with subsequent translocation to the air through vaporization and aerosolization. On the other hand, some of these open sources may be secondary emission sources to the atmosphere in that they represent the re-emission of toxic materials from open waters or land areas which have served as net sinks for the primarily emitted materials; as a result they may act as reservoirs of toxic materials for re-emission to the atmosphere under some circumstances (Eisenreich et al 1981). Murphy et al (1985), on the basis of an estimate of the atmospheric burden of PCBs over the U.S., concludes that the major sources of emission to the atmosphere have not yet been identified and speculates that secondary emissions from previously deposited PCBs on land and water could result in a cycling of these toxics between the atmosphere and open natural sinks. Such secondary emissions are unique for highly persistent contaminants and they do not attain a significance for more reactive, readily biodegradable or photolysed materials.

One of the intended applications of this toxics inventory is to provide emission inputs for models of the transport, dispersion and fates of toxic materials. In this context, the primary sources of emission, together with meteorological and other data, are the primary driving fields for the model; the subsequent depositions, accumulations and secondary remissions of toxic materials would ideally be functionally dependent output fields of a comprehensive model, were such a model available. A comprehensive model would include sub-models of the various environmental compartments: the fluxes between these compartments (including the secondary emissions to the air) would be output as a consequence of the

modelled processes. The current state of knowledge and understanding of toxic pathways in the global environment places such a comprehensive model beyond present capabilities, although significant advances are being made in modelling processes within individual compartments of the environment.

While emissions from open bodies and land surfaces are dependent on geophysical parameters, in many instances they are also strongly driven by meteorological and climatological factors. For this reason, a few isolated measurements of fluxes to the air from open sources are of limited use for directly estimating the spatially and temporally resolved emissions for the large number of toxic materials which are addressed by the present study. A feasible approach for estimating emissions from soil and water bodies which could be used for inventory preparation relies on the application of relatively simple models which include the physico-chemical properties of a solute/solvent/substrate system, as well as the dominant meteorological and climatological dependencies. The advantage of an emissions model approach is that all toxics to be considered are evaluated and their emissions estimated on a common basis.

The reliance on emission models has some attendant difficulties in that these models require concentration data in the air, water or soil media. Such concentration data, however, are more readily estimated than actual flux measurements of which only a few examples, under a limited set of conditions, are found in the literature.

8.1.1 Emissions from Soils

Primary toxic and pesticide emissions from soils result from the application of these materials directly or as contaminants to soils, road surfaces or vegetated areas. Examples are agricultural pesticide use, road dust control using PCB contaminated oil spray and brush control using herbicides. For

purposes of this discussion, soil emissions due to landfill and toxic waste disposal are not included and are considered separately.

Spencer et al (1973) provide a review of the volatilization processes for pesticides. A conceptual model of the soil/water/air interface may be described as in Figure 8.1.1. The soil void fraction is partly filled with water, the balance of the voids being occupied by air. Within the soil matrix, the toxic materials partition between solid, water and air according to their respective phase equilibria. Transport of toxics within the soil matrix has three components; molecular diffusion in air and water as well as bulk flow and dispersion in the water phase due to leaching (by irrigation, precipitation or water evaporation). At the air/soil interface, both water and toxics vapours diffuse to the air, while rainfall and dry particulates deposit toxics to the soil. Pesticides may also be applied to the surface and/or incorporated into the soil by tilling or leaching. Under strong wind conditions soil particulates and associated toxics can be entrained into the atmospheric boundary layer through turbulent mixing.

Primary soil emission rates, unlike their secondary counterparts, are mainly determined by the application rates to the soil and subsequent movement in the soil through incorporation or the processes described in Figure 8.1.1. Wet and dry depositions from the atmosphere associated with regional transport may be neglected for these primary emissions. Secondary emissions from uncultivated land, however, are directly the result of wet and dry deposition and while the soil processes play an important role, these secondary emissions are mainly in the domain of atmospheric process models and are not included in this inventory.

In Figure 8.1.1, the concentration gradient shown in solid could imply a diffusive flux of the toxic material from the soil to the air, or alternatively such a gradient might arise due to leaching of toxics incorporated into the soil. Similarly, the dotted gradient might result from application to the soil or,

alternatively, from transport to the soil surface and then to the atmosphere due to bulk water flow and evaporation ('wick' effect and efflorescence). It is clear from this brief discussion, that the behaviour of toxic materials in soils is a complex process dependent on whether the phase equilibria favour the water, air or solid phases. Furthermore, the behaviour of some toxics may have a strong dependence on the relative amounts of evapotranspiration and precipitation which will determine the seasonally variable magnitude and direction of bulk water flow within the soil matrix. While data derived from measurements of the emission fluxes of pesticides and other toxics from soils (Lewis and Lee 1976, Taylor 1978, for example) are invaluable for model development, the scope of presently available data is far too limited to permit any meaningful estimates of emissions for a wide range of toxics without the use of an emissions model.

8.1.2 Emissions from Water Bodies

Bodies of water, primarily the Great Lakes and water courses such as the Detroit and Niagara Rivers, can serve as either sources or sinks of airborne toxic materials. Figure 8.1.2 summarizes the physical processes which result in emissions and/or depositions at the air/water interface.

Emission at the surface can be due to aerosol formation or due to solute vaporization from water to air, if the fugacity difference of the solute between the two phases favours such a transfer (Mackay and Paterson 1982). Aerosol emissions result from droplet suspension and evaporation due to wind/wave interaction (Doskey and Andren 1981). Deposition to the water through wet and dry deposition of both solute and particulate materials are also indicated in Figure 8.1.2. Once in the water phase, particulate will undergo settling, adsorbing or desorbing toxic material depending on the local environmental temperatures and toxic concentrations. The sediment, which acts as a sink for its associated toxics on the floor of the lake or river,

also serves as a potential source of re-emission to water and air through the processes of resuspension and desorption.

The rate of vaporization at the water surface may be estimated using the well known principles of interphase mass transfer whereby:

$$N = K(f_w - f_a) = K(\Delta f) \qquad (8\text{-}1)$$

where N is the mass flux to air, K is the overall interphase mass transfer coefficient and Δf if the fugacity difference between the solute in the water and air calculated from the concentration and phase equilibrium (or partition) data. A fraction of the toxic material will likely be present, not as solute but, as particulate in both the air and water phases: the form of this particulate toxic will most likely be as an adsorbate on other suspended organic or inorganic material. The extent of adsorption will be dependent on an adsorption (Freundlich) isotherm which characterizes the adsorption process in either the air or water phases:

$$C \sim (\text{temperature}, w) \qquad (8\text{-}2)$$

where C is the solute concentration in the air (or water) and w is a measure of the quantity of adsorbed solute per unit area on the suspended particulate substrate. The adsorption isotherm is strongly dependent on the chemical and physical nature of the substrate material. To a good general approximation, the adsorption isotherms for trace toxics show a direct linear relationship between solute (C_w) and adsorbed phases (C_s) and the isotherm reduces to a simple partition relationship:

$$K_p = C_s/C_w \qquad (8\text{-}3)$$

In the computation of solute fugacity, proper account must be taken of the fractions of adsorbed and dissolved solute which contribute to the total phase concentration.

Resuspension processes which occur at the surficial sediment/water interface, will depend on the levels of bottom turbulence, the activity of micro-organisms in the sediment (bioturbation) and on gas convection. The bioturbation processes will likely be seasonal (Larsson 1985). Finally, in Figure 8.2 the presence of toxics in the water may be due to inflow from rivers, sewer discharges or seepage from toxic waste dumps as well as due to atmospheric deposition (Murphy and Rzeszutko 1977).

Aerosol emissions result from the entrainment into the atmosphere of droplets of water which result from bursting bubbles and splashing at the surface. Once entrained, the droplets may evaporate to residual particles containing those solutes present in the original lake water. Under unstable atmospheric conditions, these aerosol particles may be mixed throughout the atmospheric boundary layer, so contributing to the regional dispersion of toxic materials. Aerosol emissions due to the spray at Niagara Falls has been estimated to be a significant source of airborne toxics. There is some evidence that bubbles rising to the surface can also transport organics to the surface microlayer, leading to significant solute enrichment of the interface (Doskey and Andren 1981, Hoff and Chan 1987).

Foaming and splashing at the water surface is strongly dependent on the wind-imposed surface shear stress which results in the development of a spectrum of waves. Aerosol emissions will increase with high wind speeds; warm air temperatures as well as low relative humidity will also favour the rapid formation of fine suspendible particulates which would otherwise redeposit at short range. This form of toxic emission is dependent on the concentration in the surface water and the rate of suspended aerosol formation.

It is clear from this brief discussion of the various processes which affect the interphase transfer of airborne toxics to or from water bodies that, depending on the prevailing air and water concentrations, the lakes can act as either sources and/or sinks for airborne toxics. To resolve the net effect of the various processes summarized in Figure 8.1.2 would require a comprehensive model of the water body.

From a review of the literature, it is concluded that the deposition and emission from lakes and rivers is the subject of ongoing research and a general methodology for computing emission factors does not exist. In some cases, scientific opinion is divided on whether individual lakes and rivers serve as atmospheric sinks or sources. For some toxics such as PCB and dioxins, there is evidence that particulate sedimentation rapidly strips these toxics from the water column, implying that water bodies act as sinks for these materials. In view of the lack of sufficient understanding of many of the processes which will have a major influence on emission estimates from water bodies, emissions from these sources have not been estimated.

Figure 8.1.1
Soil and Atmospheric Processes which Determine Volatilization of Soil Applied Toxics

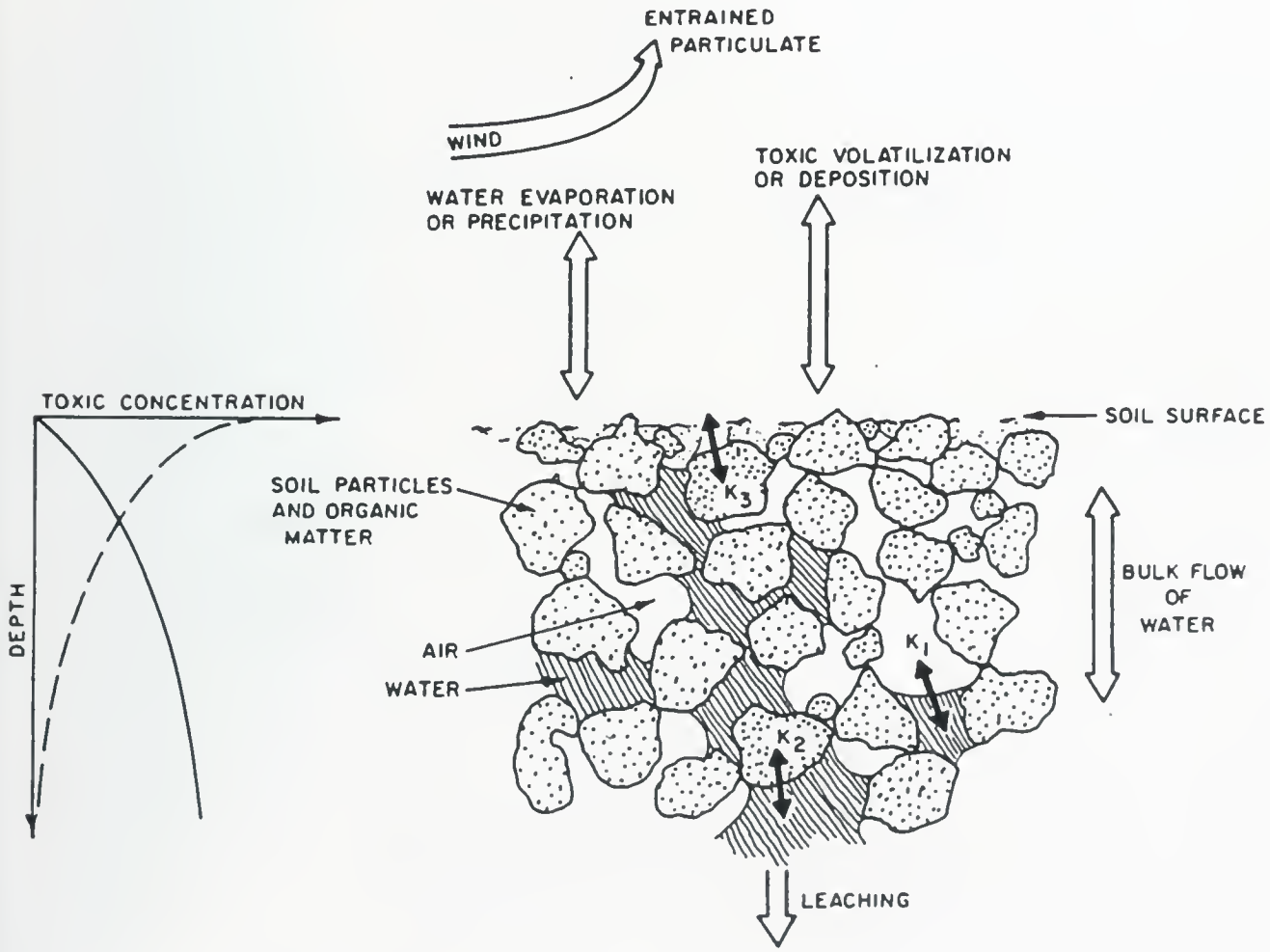
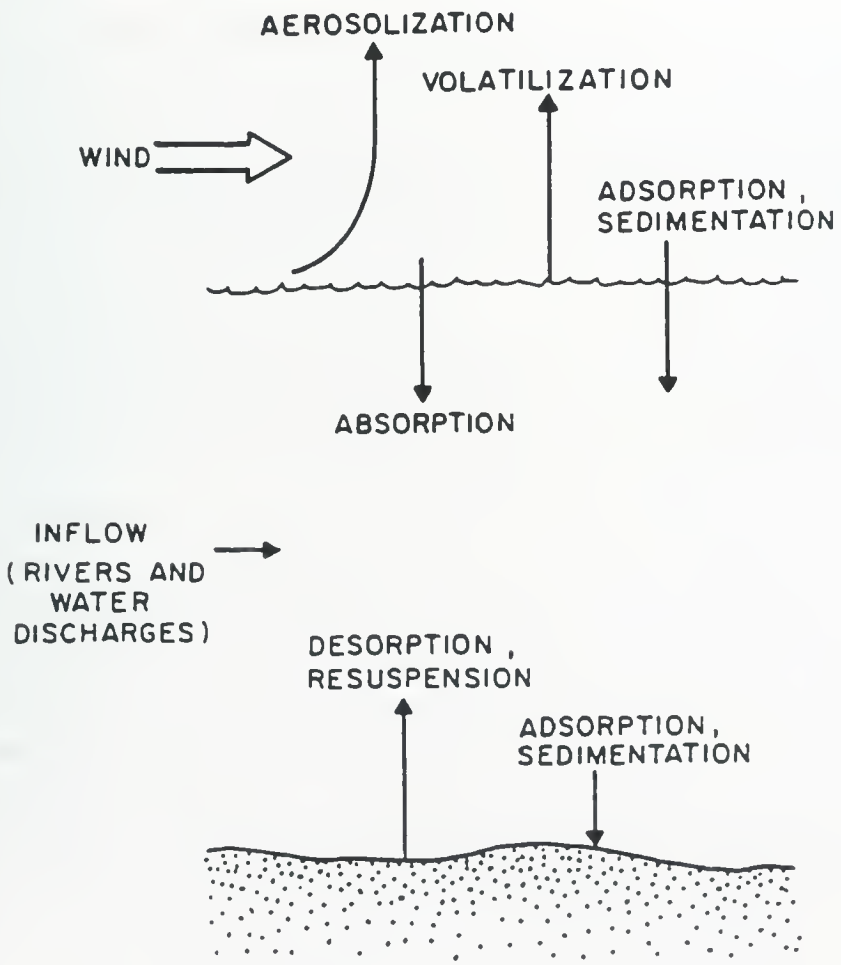


Figure 8.1.2

Processes Resulting in Emissions and/or Depositions at the Air/Water Interface



8.2 Pesticide Emissions from Agricultural Use

The components of emission to the air resulting from agricultural use of pesticides are application losses through volatilization from vegetation and soil, and resuspension of toxics in association with wind blown dust.

8.2.1 Models as Emission Algorithms for Toxics from Soils

Leistra (1973) provides a general overview of the requirements and approaches in modelling the volatilization of pesticides from soils. Both analytical and numerical procedures are discussed. Several analytical solutions are provided for estimating the transient behaviour of vaporization under several idealized soil conditions. Jury et al (1983) proposed a behaviour assessment model for trace organics in soil. The model comprises the analytical solution of the time dependent mass balance equation for toxics which includes the processes described in Figure 8.1.1. This analytical model assumes that the aerodynamic resistance for volatilization and the properties of the moist soil matrix remain constant, and that the water evaporation rate or precipitation rate is such that the hydraulic flux of water through the soil is constant. Jury emphasizes that this is a screening model for pesticides behaviour in soils rather than a scenario model for simulating time variable field conditions. In three subsequent papers (Jury et al 1984 a, b, c) the model is further explored and evaluated against volatilization data; the good agreement between modelled and observed volatilization rates indicates that this analytical model is a reasonable representation of the important processes leading to toxic emissions from soils. The model was used to examine the behavior of 35 pesticides and other chemicals (Jury 1984b) and tested against vaporization data for seven pesticides in a variety of soil types, with different moisture and organic contents (Jury 1984c).

Eduljee (1987) used an algorithm based on the Jury et al model to estimate the volatilization of PCB and TCDD from soil: from this study it was concluded that volatilization fluxes for TCDD and Aroclors 1242, 1254 and 1260, calculated from the model, are in qualitative agreement with observations from field and laboratory experiments.

For the present inventory preparation, the Jury model has been selected on which to base an emissions algorithm. This model has the advantage of being simple, even though it is restricted to constant soil moisture and evaporation rate. The Jury model can readily be used to estimate the average volatilization emissions to the atmosphere using climatological evaporation rates and soil conditions, appropriate to the season and geographical location. Using the Jury model in this manner as an emission algorithm gives an assessment of the relative importance of a wide range of toxic materials in soils and provides a reasonable estimate of emission rates considering the large uncertainties in soil concentrations, physico-chemical properties and other parameters on which soil emissions depend.

8.2.2 Development of an Emission Factor Algorithm for Volatilization from Soils

The Jury analytical expression for the volatilization flux from soils is:

$$J_s(0,t) = 1/2\, C_0 \exp(-kt)[V_E\{\mathrm{erfc}(V_E t/\alpha) - \mathrm{erfc}(L/\alpha + V_E t/\alpha)\}$$

$$+ (2H_E + V_E)\exp[H_E(H_E + V_E)t/D_E]\cdot$$

$$\cdot\{\exp(H_E L/D_E)\mathrm{erfc}[L/\alpha + (2H_E + V_E)t/\alpha] - \mathrm{erfc}[(2H_E + V_E)t/\alpha]\}] \qquad (8\text{-}4)$$

where: $J_s(0,t)$ = volatilization flux (kg/m^2-d)

C_0 = initial soil concentration of solute incorporated uniformly to a depth of L (kg/m^3)

t = time since application (days)

L = incorporation depth (m)

k = chemical/biological decay rate ($days^{-1}$)
V_E - function of soil water flux (m/day)
D_E = volume average effective solute diffusivity (m^2/day)
H_E = aerodynamic bulk transfer coefficient to air (m/day)
α = $4D_Et$

The parameters V_E and L which depend on the climatology, irrigation practice and pesticide application method, are important parameters in determining the soil emission flux for many of the pesticides being considered in this study.

8.2.2.1 Soil Water Flux

In the absence of irrigation, climatological estimates of the soil water flux can be obtained from monthly average solar radiation flux at the surface and the monthly mean temperature (Priestley and Taylor 1972, Davies and Allen 1973), whereby:

$$E_w = \beta(s/(s + \gamma)) \cdot (Q_N - Q_s) \qquad (8\text{-}5)$$

where E_w is the mean monthly evaporation flux (W/m^2), Q_N is the net radiation flux, Q_s is the soil heat flux (neglected in this study), $\beta = 1.26$ for cropped surfaces, γ is the psychrometric constant and s is the slope of the water vapour pressure curve. The difference between the estimated evaporation and the monthly precipitation is the net soil water flux. All inputs are mean monthly values which were obtained from climate atlases for the U.S. and Canada. The net radiation in Canada, however, was estimated from station data available for Winnipeg, Churchill, Toronto, Ottawa, Schefferville, Montreal, Fredericton and St. John's. The net soil water flux was estimated on a monthly basis for each state and for the southern regions of each province in the grid. Thereafter, the monthly values were

averaged to provide seasonal estimates for use in the volatilization flux algorithm. Figure 8.2.1 shows the total 1985 monthly average precipitation and evapo-transpiration at Pearson International Airport (Toronto). The following table based on this figure, shows the mean monthly and seasonal water flux derived as the difference between the totals of precipitation and evapotranspiration.

		Monthly Mean Water Flux (mm/day)	Seasonal Mean Water Flux (mm/day)
Winter	December	-	
	January	-	-
	February	-	
Spring	March	-1.4	
	April	-0.6	-0.3

		Monthly Mean Water Flux (mm/day)	Seasonal Mean Water Flux (mm/day)
Summer	June	+1.8	
	July	+1.5	+1.3
	August	+0.8	
Fall	September	-0.3	
	October	-1.4	-1.3
	November	-2.1	

On a seasonal basis, precipitation exceeds evapotranspiration for all but the summer season (June/July/August) and the soil water flux is accordingly negative (leaching). For the summer season, the total net soil water flux is positive at approximately 134 mm or 1.3 mm/day excess evapotranspiration over precipitation. The peak monthly upward water flux is in June at 1.8 mm/day. During spring, maximum soil leaching occurs in March with a downwards water flux of 1.4 mm/day. During the winter months, when the ground is frozen, the water flux is essentially zero; the accumulated precipitation appears in early spring as runoff rather than as water flux to the soil.

In southern Ontario, the application of pesticides to cultivated lands occurs mainly in the period May to September. For the summer months of this period, the water flux is positive with an average value of 1.3 mm/day. The September water flux is downwards at -0.3 mm/day.

8.2.2.2. Compilation of Physical/Chemical Properties

The data required in the computation of volatilization using the Jury et al (1984) model, includes estimates of the partition of the selected pesticides between the solid, water and air phases which make up the soil matrix. The extent of adsorption on the solids is mainly determined by organic carbon content of the soil and the soil water partition may be conveniently estimated from the partition of the pesticide between octanol and water. At the trace concentrations which are of concern here, the partition between water and air can be described by Henry's Law coefficient, (K_h). Directly measured data for air/water partition are sparse. Assuming ideality, however, Henry's coefficient may be estimated from the solute vapour density and water solubility; these data are far more abundant, although data are generally for a single temperature in the range 20-25°C. The temperature dependence of the partition coefficients is consequently, not generally available for most of the compounds considered in this study.

From a review of reported values of vapour pressure, solubility and octanol/water partition, it is apparent that the uncertainty in these data (factors of ten or more in many cases), is likely comparable or even in excess of the expected magnitude of variation due to temperature. No attempt has been made in this study to include temperature dependance of the partition coefficients.

The pesticide data which are required for the Jury model are:

- octanol/water partition coefficient (K_{ow})
- Henry's coefficient (K_h), or both the vapour density and solubility
- degradation half-life of the pesticide in the soil due to chemical or biological activity

These data have been extracted from a number of sources. Suntio et al (1987) have reviewed the literature for a large number of pesticides and other toxic organics. They have selected values of K_{ow} and have derived K_h from solubility and vapour pressure values which they consider to be the most reliable data. These values have been used in this study. For those pesticides not reviewed by Suntio et al, other published data have been used and in two instances, K_{oc} was estimated from the water solubility using the empirical relationship of Karickhoff (1981):

$$\text{Log}_{10}(K_{oc}) = -0.594\ \text{Log}_{10}(X_s) - 0.197 \qquad (8\text{-}6)$$

where X_s is the solubility in water expressed as a mole fraction. The organic carbon partition coefficient, K_{oc}, was estimated from:

$$K_{oc} = 0.41\ K_{ow} \qquad (8.7)$$

(Karickhoff, 1981). Finally, the soil water partition, Kd, is expressed in terms of the soil organic carbon fraction, f_{oc}, as:

$$K_d = f_{oc}K_{oc} \quad (8\text{-}8)$$

Table 8.2.1 lists the values of K_{oc}, K_h and $t_{1/2}$ used for the present emission estimates. Most of the $t_{1/2}$ data are from Jury et al (1987), Edwards (1975) and National Research Council Canada (NRCC) reports on the specific pesticides.

Two further properties required for the emissions estimates are the molecular diffusivity of the solute in air and in water. Data for these properties are not generally available for the pesticides being studied. For the present purposes the following typical values used by Jury et al (1987) and Eduljee (1987) have been adopted:

D_{air} = 0.43 m^2/day
D_{water} = 4.3 x 10^{-5} m^2/day

8.2.2.3 Soil Properties

Soil properties which are typical of cultivated agricultural land are required by the Jury algorithm. Since the soil texture of cultivated lands is generally somewhat modified by tilling practices and fertilization, the regional soil texture and moisture are not necessarily descriptive of crop lands. Jury et al (1984) have examined the sensitivity of volatilization fluxes to soil moisture and organic carbon content. Solutes which partition strongly to water rather than the air phase, (low K_h), are most sensitive to soil moisture, although their volatilization rates are also typically low. When soil moisture was varied from near the wilt point to soil saturation moisture, the flux decreased by a factor of 10 in their sensitivity study. Typically, soil moisture variations in agricultural lands would not approach these extremes, particularly where irrigation is practiced. Sensitivity to organic carbon fraction was found to be somewhat greater, approaching a factor of 100 for a range of f_{oc} from 0.005 to 0.05. Again, cultivated soils would not be expected to have such a large

range of carbon content; a factor of 10 variation in the flux is more likely, corresponding to a f_{oc} range from 0.01 to 0.04.

For purposes of emissions estimates, the following soil parameters are assumed typical of agricultural cultivated soils:

soil moisture fraction (θ)	=	0.3
organic carbon fraction, f_{oc}	=	0.0125
soil bulk density ρ_b	=	1350 kg/m^3
porosity ϕ	=	0.5 m^3/m^3 soil

8.2.3 Estimation of Pesticide Loading to Soil and Vegetation

Pesticide applied to agricultural land can follow several different paths. If the soil is bare (pre-emergent application) and the pesticide is surface applied or soil incorporated, then the entire applied amount is considered to be loading to the soil for emission rate estimation. On the other hand, if the pesticide is used to spray fruit trees, only a small fraction of the application reaches the soil, the remainder being retained by the primary target or is deposited as drift on surrounding vegetation. Post-emergent application will also impact both soil and vegetation. The penetration of the pesticide through the crop cover to the soil will depend on the crop growth stage or the leaf area index which is a measure of the leaf area per unit area. The plant coefficient can be considered to be an interception index or shading factor which varies from zero for bare soil to near 1.0 for dense vegetative cover. Willis and McDowell (1987) have compiled representative literature values for the interception by crop and other target surfaces of aerial and ground applied pesticides. The data show that 62% (standard deviation 27%) of the ground applied pesticide is intercepted by the target, while the corresponding figure for aerial application is 45% (s.d. = 20%). These data are consistent with a shading factor in the approximate range of 0.25 to 0.89.

For present purposes, the following shading factors are assumed:

Winter	0.04
Spring	0.30
Summer	0.78
Fall	0.19

Hence, the maximum interception of applied pesticide by the vegetation is assumed to be 78 percent in the summer, while in the winter 4 percent interception is assumed in those southern states where the growing season persists into the winter season. Pesticide intercepted by the vegetation is available for volatilization or wash-off to the soil.

8.2.4 Computation of Emission Factors

The four components of pesticide emission addressed in this section are:

- volatilization from soils
- volatilization from vegetation
- wind erosion of soil
- drift losses during application

8.2.4.1 Volatilization Emissions from Soils

Emission factors for pesticides incorporated into the soil have been estimated using the Jury model by computing the monthly average volatilization flux for each month following a loading of 1 kg/ha of the pesticide to the soil. Values for two soil incorporation depths, 1 cm and 10 cm, have been computed for water flux values of 2.5, 1.25, 0.0, -1.25, and -2.5 mm/day. The 1 cm incorporation simulates spray or other surface application while a 10 cm incorporation depth is consistent with application in-furrow during planting or tilling. The Jury model is linear in the areal rate of application and the emission factors are expressed as kg/ha-day per kilogram applied pesticide/ha. The results of these computations are

presented graphically in Appendix A. In compiling the emissions inventory, factors for intermediate water fluxes were obtained from the plots by interpolation.

Figures 8.2.2 and 8.2.3 show the emission factors for the herbicides alachlor and atrizine incorporated to a depth of 1 cm. Comparing these figures for E = +1.25 mm/day, it is seen that the monthly mean emission flux for alachlor falls by almost two orders of magnitude by the fourth month following application, while that for atrizine decreases by a factor of only two. The initial monthly mean emission factors for the month following application are approximately 6×10^{-3} and 1.6×10^{-3} kg/ha-day, respectively. After four months (May to August in Figure 8.2.1, for example), the factor for alachlor has fallen to 7×10^{-5} while the emission rate for atrizine is an order of magnitude higher at 6×10^{-4} kg/ha-day. In the fifth month, September in our present example, the water flux is negative (-0.3 mm/day) and it can be seen that residuals of either herbicide are rapidly leached from the surface and emissions fall to insignificant values.

Figures 8.2.4 and 8.2.5 contrast the very different behaviors of the insecticides methoxychlor and carbofuran incorporated to a depth of 1.0 cm. Methoxychlor partitions strongly in favour of the stationary organic carbon soil component and as a consequence is relatively immobile within the soil regardless of the water flux. The emission factor over a period of five months declines from an initial value of 3.5×10^{-3} to 7.0×10^{-4} kg/ha-day. With an estimated degradation half-life of 1-year, methoxychlor is expected to be persistent in soils with approximately 50% persisting to the following year. Carbofuran, on the other hand, behaves in a manner similar to to alachlor and emissions rapidly decrease over a period of five months. With a degradation half-life of 40 days, carbofuran is not expected to persist from year-to-year. Mancozeb and metiram are essentially non-volatile pesticides and are, therefore, not considered in this emission pathway.

For pesticides with relatively short decay times, or those which are rapidly leached or volatilized from the soil (see Figures 8.2.2 and 8.2.5 for alachlor and carbofuran for example) reasonable seasonal estimates of the emissions to the atmosphere can be made by using the cumulative loss to the atmosphere over a three month period during the season in which the pesticide was applied. For persistent pesticides (see Figure 8.2.4, methoxychlor, for example) the volatilization from the soil continues for many months after application and soil emission rates will be somewhat underestimated for sparse vegetation cover. In the summer season, however, the volatilization of pesticide intercepted by the vegetation is the major loss route to the atmosphere, making the details of the soil volatilization less important. The soil emission factor for all seasons was, therefore, based on the three month cumulative volatilization determined by the Jury model, using the seasonal mean soil water flux for the state or provincial region.

8.2.4.2 Emission Factors from Vegetation

Studies of the rate of disappearance of applied pesticides from target vegetation have shown that the major loss routes are generally volatilization and wash-off by rainfall (Willis et al 1985). The post-application meteorological conditions such as temperature, humidity, wind, solar radiation and precipitation will have important effects on the rate of loss and on determining which of the major loss routes dominates. Willis et al (1985) showed that without precipitation, 50% of applied toxaphene, methyl parathion and fenvalerate was lost from cotton plants in 0.7, 0.1 and 3.3 days, respectively. Taylor (1978) reports that 90% of dieldrin was lost from orchard grass in 30 days. Other studies (Lewis and Lee 1976, Ritcey et al 1981, for example) have shown that the loss rates of pesticides from vegetation are vapour pressure dependent and have time scales of the order of days: this is short when compared to the overall seasonal resolution of the present inventory. Wash-off rates to soil appear to be

related to cumulative precipitation with 35% of applied permethrin being washed off cotton plants in 2 hours by 25 mm of rain. An additional 76 mm of rain removed a further 11% (Willis et al 1986).

In an averaged sense, the relative volatilization and wash-off amounts will depend on the volatilization half-life and the dry period following application before rain occurs.

Data on the persistence half-lives of pesticides deposited on a wide variety of crops have been compiled by Willis and McDowell (1987). Half-lives are categorized into persistence of dislodgeable residue and total residue. The former residue is removed by water and detergent or by 15 to 60 seconds of extraction with an organic solvent. The total residue is obtained by long-term extraction which removes both surface and internal residues.

Table 8.2.2 is a summary of data extracted from the above study for pesticides of present interest. Only the half-life range has been given in Table 8.2.2 with no distinction between dislodgeable and total residues. The Willis and McDowell study results indicate that wash-off by rain leads to a half-life which is comparable to that without rain. Under dry conditions loss is dominated by volatilization. It is apparent from the results in Table 8.2.2 that on a seasonal scale, essentially all of the pesticide deposited on the vegetation is lost. Generally, pesticide application is planned when the probability of rain events is low. Based on the half-lives reported by Willis and McDowell, in the span of 5 to 10 days, 50 to 75% of the pesticide on the vegetation will in general be emitted to the atmosphere. For purposes of this inventory, it is assumed that 70% of the pesticide impacting the vegetation volatilizes and the remaining 30% is transferred to the soil by wash-off or other mechanism. Figure 8.2.6 summarizes the fate of pesticide applied to vegetation which has been used for this inventory. Again, metiram and mancozeb are regarded as non-volatiles and are not considered.

8.2.4.3 Pesticide Associated with Wind Blown Dust

Suspended particulate emission from tilled agricultural fields is readily estimated using methods reported in AP-42 (U.S. EPA 1985). The toxic material associated with the suspended dust depends on the concentration of adsorbed toxic in the surface soil: this concentration can be estimated using the Jury et al (1983) model described in Section 8.2.3. The emission of pesticide associated with windblown dust, however, will only be a significant route to the atmosphere (when compared to volatilization from soil and vegetation) for highly persistent pesticide residues; this is especially true of pesticides that have been discontinued. Dust associated emissions will be most significant during tilling and in the early growing season. There are insufficient data on the residues of discontinued pesticides in agricultural soils to enable a meaningful estimate of this emission route to the atmosphere. Persistent pesticides in this discontinued category are aldrin, dieldrin, endrin, mirex, DDT and toxaphene.

8.2.4.4 Pesticide Application Drift Losses

Drift loss of pesticide refers to that portion of the applied amount which does not deposit in the intended target area. Such drift can comprise some 30% or greater of the applied material, depending on application method (i.e., aircraft or spray boom) and prevailing meteorology. Pesticides applied as dusts are in some instances more prone to drift than liquid aerosols, due to the fine particle size fraction present in some crop dusts (Lewis and Lee 1976). While the off-target drift of insecticides and herbicides represents a major input of these materials to the air, the physical form of the emission (particulate or vapour) will depend on the vapor pressure. If the vapour pressure is greater than 10^{-7} mm Hg, then emissions are primarily vapour (Seiber and Woodrow 1983): most pesticides are in this category. The short term impact of drift deposition in populated or other areas is generally of limited range when compared to volatilization. For example, Miller (1980)

analysed fixed-wing spray data for trichlorpyrifos, 2,4,-D/picloram and 2,4,5-T/picloram. These results indicate that between 72% and 82% of the application impacted the target area and 99% or greater impacted within approximately 500 m. Once deposited either on or off-target, a percentage of the applied pesticide, which is large when compared with long range drift, may enter the atmosphere through volatilization. Other studies suggest that under some meteorological conditions the drift impact range is greater: in a 1979 New Brunswick study, fenitrothion emulsion with a dye tracer was sprayed over spruce forest . At 1.2 km downwind, under unstable conditions, no drift was observed while an estimated 10% of the material was still airborne under stable conditions.

The highest grid resolution of the MOE variable grid is 5 km. With this resolution, off-target drift emissions within the grid will, to a large extent, redeposit and/or volatilize within the same grid: in this context, particulate drift emissions to the atmosphere are mainly sub-grid scale and do not constitute a separate emission routes for this inventory.

8.2.4.5 Formulation of an Overall Emission Factor for Pesticide Use

From the foregoing discussion, the overall emission of pesticide to the atmosphere is via volatilization from the soil or direct volatilization from vegetation. In instances where the pesticide is soil incorporated to approximately 10 cm before planting, only soil volatilization is considered. Some pesticides are applied both through soil incorporation and as a pre or post-emergence surface application. In such instances, the relative amounts applied in each manner are assumed equal. From the volatilization routes shown in Figure 8.2.6, the following overall seasonal emission factors for pesticide application are derived:

Surface application only (1 cm depth)

$$E_1 = 0.7\sigma (1 - f_1) + f_1 \qquad (8\text{-}9)$$

Soil incorporation only (10 cm depth)

$$E_{10} = f_{10} \quad (8\text{-}10)$$

Both soil incorporation and surface application (each 50%)

$$E_{1,10} = (f_1 (1 - 0.7\sigma) + 0.7\sigma + f_{10})/2 \quad (8\text{-}11)$$

where E_1, E_{10} and $E_{1,10}$ are the overall emission factors for surface application, soil incorporation and a combination of these two modes, respectively. The individual soil emission factors f_1 and f_{10} are the fractions of applied pesticide volatilized from soil over a three month period for surface application and soil incorporation. In calculating f_1 and f_{10}, the appropriate seasonal average soil water flux for the state or provincial region is used in the Jury model.

8.2.5 Compilation of Pesticide Usage Data

8.2.5.1 Agricultural Application

In view of the widely different properties of the pesticides in agricultural use, it is necessary for purposes of estimating emissions to examine each pesticide separately and to apply an emission factor which is specific for the pesticide and its use pattern. Shoakat et al (1985) have reviewed the sources of data relating to pesticide use in Canadian agriculture and many of the sources were obtained from this document.

Defining the season and mode of application for each pesticide is difficult to generalize, since use pattern depends on the crop and the geographical location. The Ontario Ministry of Agriculture and Food publishes several annual guides for fruit, vegetables and other field crops (Ontario Ministry of Agriculture and Food 1988 a,b,c; 1989 a,b). These publications have been reviewed and Table 8.2.3 has been drawn up giving general estimates of

the mode or modes of application as well as the fractional use in each season. The estimates in this table have been used for all provinces as well as the United States, except for Texas, Mississippi, Louisiana and Florida. For these states, the winter period has monthly average temperatures in excess of 5°C and some pesticide use is assumed in the winter season as is reflected in Table 8.2.3. Where both surface and soil incorporation of a pesticide are indicated in the table for a season, it is assumed that applications are equally divided between these two modes.
Compiling data on individual pesticide use has proven a most difficult task in this study. The pesticide market is highly competitive and as a result, all data provided by manufacturers and formulators to the Canadian or U.S. Governments (with few exceptions), is held strictly confidential and is, therefore, unavailable for this inventory work. The various government agencies do, however, publish summaries of pesticide sales on either a provincial, hydrographic (water-shed) or county basis. These summaries, however, are prepared in a manner designed to confound any attempt to reconstitute the sales figures (and therefore useage) for a specific active ingredient.

For purposes of this inventory work, inferential methods had to be developed, based on the limited published data, which have enabled the gridding of pesticide use in Ontario, Quebec and the Atlantic provinces, according to active ingredient. The details of these estimation methods are provided in Section 8.2.6 and only an overview and summary of the results is given in this Section.

Fortunately, it is possible to do a global (provincial total) cross-check of the method for specific pesticides and pesticide groups, using the few non-confidential 1985 sales figures. These cross-checks suggest that the method yields results within a factor of better than four for specific ingredients in the Atlantic Provinces (grouped) (Table 8.2.4) and considerably better than a factor of two in Quebec. Footnotes to the table

indicate some of the anomalies. The methods do not give a good estimate for chlordane or lindane. The sales of these two pesticides reported at source, far exceed the retail sales for agricultural use. The major use of chlordane is in soil treatment around buildings and structures against termites, and its agricultural use is minor as indicated in the tables. Lindane is extensively used for seed treatment and as such, the retail sales of active ingredients would not reflect this application route to the soil.

Table 8.2.4 also compares the non-confidential total 1985 sales for Ontario with the results of a 1983 farm survey by Ontario Ministry of Agriculture and Food. Provincial totals based on the OMAF survey (even though for 1983) provide a more direct comparison between use statistics and sales. Again, sales of chlordane and lindane do not reflect in the agricultural use figures due to seed treatment (lindane) and non-agricultural use (chlordane).

Reviewing Table 8.2.4, it is also noted that the herbicide 2,4-D is underestimated in Ontario and the Atlantic provinces, but overestimated in Quebec. Diazinon shows a bias towards underestimation by a factor of 2-3.

8.2.5.2 Home and Garden Application

A 1982 analysis of the pesticide industry in Canada (Industry, Trade and Commerce 1982) provides the following breakdown of pesticide end-use:

	Canada 1982	U.S. 1982
Agriculture ($)	93.2%	63.3
Industry/Commerce/Government ($)	5.7%	25.0
Household ($)	1.1	11.7
	100.0	100.0

A more recent analysis for Canada (1988) as provided by Onderdank

(private communication 1989) is as follows:

Agriculture ($)	82.5%
Home and Garden ($)	10.0%
Industrial ($)	5.5%
Forestry ($)	1.0%
	99.0

Based on these analyses, the amount of pesticides in household use is 10% or less of the total consumption. In view of the uncertainty inherent in the methods used for estimating pesticide use, the relatively small percentages used industrially, in households or for forestry cannot be resolved in this study.

8.2.6 Details of the Estimation Methods for Gridded Application Rates of Specific Pesticides

Due to the sparseness of detailed pesticide use data, different methods of deriving application rates for individual pesticides had to be developed for Ontario, other provinces and the United States. The methods used are detailed in the following sub-sections.

8.2.6.1 Ontario

The most recent and complete data available to this study for Ontario is the 1983 Ontario Ministry of Agriculture and Food (OMAF) farm survey of pesticide use (McGee 1984). The survey is based on a questionnaire mailing to 10,000 farms (field crops) and 1450 fruit and vegetable producers. Response rates of 30% (3000) and 38% (560), respectively, were achieved.

For field crops the sample data set was expanded by McGee to a county level, and drainage basin level, and finally to a provincial estimate on the basis of the sampled acreage and total acreage by crop. For fruit and

vegetable application, the provincial total was first estimated on the basis of the survey and then disaggregated to county and drainage basin level.

The final estimates are reported by McGee in several formats. County and drainage basin data are provided according to generic pesticide type without resolving the specific pesticides by compound name. Use data by compound name are provided as Ontario totals for all agricultural uses and roadside spraying, as well as provincial totals by crop application. The latter active ingredient data were used in the present study to prepare compound profiles for each generic group. For instance, kilograms of triazine herbicides were speciated into separate quantities by atrazine, cyanazine, simazine and metribuzine according to crop. Crop acreage data by county was then used to allocate drainage basin data (for generic pesticide groups) to counties for each specific active ingredient. The county data were then gridded to the UTM grid by area apportionment.

8.2.6.2 Quebec

The most recent and complete data for Quebec are provided for the year 1982 by Environment Canada (Reiss and Paré 1984). This report details the results of a census of pesticides sold to Quebec farmers in 1982. The data are reported on the basis of six regions, which are further sub-divided into 126 watersheds. To preserve the confidentiality of the sales data, the quantities of individual active ingredients were totalized into 22 generic groups of which the following nine are relevant to the present study.

Generic Group	Pesticides in Group
Carbamates	carbaryl carbofuran butylate mancozeb metiram 19 others*

Organophosphates	diazinon 29 others*
Phthalimides	captan 2 others*
Aryloxyacids	2,4-D 2,4-DB MCPA 6 others*
Triazines and triazoles	atrazine cyanazine metribuzin 4 others*
Amide derivatives	alachlor metoalochlor 7 others*
Substituted ureas	linuron 6 others*
Organochlorines	chlordane chloropicrin dichloropropanes dichloropropenes endosulfan lindane methoxychlor 4 others*
Miscellaneous	methyl isothiocyanate trifluralin 16 others*

* Pesticides not included in this inventory.

In order to arrive at an estimate of pesticide emissions from agricultural use, it is essential to devise a method of speciation of the total pesticide in each generic group into separate pesticide amounts. This was done by

assuming that the profile of the percentages of each active ingredient included in each generic group, after some adjustment for crop mix, was the same as the Ontario profiles. With this assumption, the speciation profiles were calculated using the 1983 OMAF study for Ontario. Applying the Ontario speciation profiles to the total of each generic group for each of the 126 watersheds in Quebec, provided an estimate of the geographical distribution of each active ingredient in the province.

The organochlorine group of pesticides required some additional analysis since this group is Ontario is dominated by the large amounts of soil sterilants used (approximately 94%). These sterilants, comprising chloropicrin, dichloropropane and dichloropropene are used almost entirely for tobacco culture. The other Ontario crop which has a strong influence on the profiles of active ingredients is soybeans, for which the largest herbicide active ingredient is metribuzin. Soybean acreages in Quebec are small compared to Ontario. Unless allowance is made for the differences in tobacco and soybean acreage, the sterilants and metribuzin would be greatly overestimated in Quebec. The speciation profiles were accordingly computed without those pesticides, which are associated with tobacco and soybeans and the provincial total methoxychlor use in Quebec computed. The difference between this methoxychlor total and the non-confidential 1985 Quebec sales total was assumed to be due to tobacco culture in Quebec, so enabling an estimate of the sterilant use.

A comparison of the results of this estimation method for individual active ingredients with non-confidential 1985 Quebec sales (Table 8.2.4) show that the estimates agree with the actual sales volumes to better than a factor of two, except as noted in the table for chlordane and lindane. This lends confidence in using the estimates for other pesticides for which the sales figures are confidential. The watershed data were gridded to the 127 km modelling grid by area apportionment.

8.2.6.3 New Brunswick

A published 1985 census of individual pesticide active ingredients sold in New Brunswick form the basis of the inventory data in this province (Shanks 1985). The data are reported in terms of kilograms of active ingredient sold within the province without any geographical distribution. The inventory grid resolution outside Ontario is 127 x 127 km, making the province of New Brunswick about two grid cells wide.

Since the regions of agricultural acreage and major crop types within the province are quite well defined using the National Atlas of Canada (1974), the allocation of pesticide use to the inventory grids was done on the basis of crop type and agricultural area.

8.2.6.4 Prince Edward Island and Nova Scotia

For both these provinces, 1986 surveys of pesticides sold for agricultural purposes are available (Environment Canada 1986a, Environment Canada 1988). Survey data are reported as provincial totals of 16 generic pesticide groups. In this report, the tasks of deriving the sales of individual active ingredients is similar to that in Quebec, where only grouped pesticide data are available.

Exactly the same methodology used for Quebec, was applied to the Nova Scotia and Prince Edward Island data. Using the 1985 New Brunswick census of active ingredients, speciation profiles were computed for each pesticide group and then applied to the group data in these other two provinces. In this manner, estimates of the quantities of individual active ingredient sold were made. Table 8.2.4 compares the Atlantic province totals of non-confidential 1985 sales with the present estimates. The ratios of estimate/1985 sales show some differences of a factor of 3 or 4, with a bias towards underestimation, particularly for the herbicides 2,4-D and

MCPA. The greater uncertainty in the Atlantic Provinces results could be due to the smaller sales volumes and farm stocked pesticides could represent a larger fraction of the sold volumes. The pesticide use estimates were transferred to the 127 km grid by area apportionment.

8.2.6.5 United States

Gianessi and Puffer (1988) have prepared an inventory of pesticide use in the U.S. by state for "a year circa the mid 1980's". The data for 25 selected pesticides were extracted from publicly available reports from federal and state governmental agencies. The following ten pesticides included in their data base were relevant to the present study:

2,4-D	cyanazine
alachlor	diazinon
atrazine	metolachlor
carbaryl	trifluralin
carbofuran	

State totals for the use of these ten pesticides were allocated to the 127 km modelling grid using agricultural land area as a surrogate quantity.

TABLE 8.2.1

Pesticide Properties

	K_{oc} (m^3/kg)	K_h	$t_{1/2}$ days
Herbicides:			
2,4-D	2.0×10^{-2}	2.26×10^{-4}	15.
MCPA	3.4×10^{-2}	2.0×10^{-8}	22.
Alachlor	2.6×10^{-1}	2.6×10^{-6}	18.
Atrizine	1.03×10^{-1}	1.19×10^{-7}	71.
Butylate	1.05	2.3×10^{-4}	30
Cyanazine	1.9×10^{-1}	1.2×10^{-10}	14.
Linuron	6.5×10^{-2}	2.2×10^{-6}	75.
Metolachlor	1.37×10^{-1}	3.2×10^{-7}	42.
Metribuzin	2.4×10^{-2}	9.5×10^{-8}	37.
Trifluralin	4.1×10^{-1}	1.7×10^{-3}	132.
Insecticides:			
Aldrin	4.1×10^{-1}	3.8×10^{-2}	120.
Carbaryl	8.2×10^{-2}	5.3×10^{-7}	22.
Carbofuran	1.6×10^{-2}	2.1×10^{-7}	40.
Chlordane	4.1×10^{-1}	3.7×10^{-3}	365.
Dieldrin	2.1×10^{-0}	4.6×10^{-4}	840.
Diazinon	8.2×10^{-1}	2.8×10^{-5}	32.
Endosulfan	1.63×10^{-0}	1.2×10^{-3}	800.
Endrin	6.5×10^{-1}	1.4×10^{-5}	800.
Lindane	2.6×10^{-0}	5.3×10^{-5}	350.
Methyoxychlor	$8.4 \times 10^{+1}$	5.5×10^{-3}	365.
Mirex	$3.26 \times 10^{+3}$	3.5×10^{-1}	800.
DDT	$4.1 \times 10^{+2}$	9.7×10^{-4}	3800.
Toxaphene	8.2×10^{-1}	1.7×10^{-4}	365.
Fungicides and Fumigants:			
Captan	2.6×10^{-2}	2.5×10^{-4}	5.
Chloropicrin	$9. \times 10^{-2}$	8.1×10^{-2}	30.
Dichloropropanes	5.5×10^{-2}	1.2×10^{-1}	16.
Dichloropropenes	6.6×10^{-2}	1.5×10^{-1}	16.

TABLE 8.2.2

Extracted from Willis & McDowell (1987)
Persistence Half-lifes on Vegetation

	v.p.(Pa)*	$t_{1/2}$ (days)	Crop
Aldrin	3.6×10^{-2}	1.7	Alfalfa
Chlordane	7.9×10^{-3}	2.3	Kale
DDT	1.5×10^{-4}	1.6 - 18.8	Alfalfa, Cotton, Collards
Dieldrin	1.9×10^{-2}	2.7 - 6.8	Alfalfa, Grasses, Peach
Endrin	1.5×10^{-3}	3.3 - 7.0	Alfalfa, Trefoil
Endosulfan	5.0×10^{-3}	0.9 - 4.9	Grape, Pear, Cotton, Endive, Tobacco, Alfalfa, Beets, Chard, Collards, Lettuce,Turnip
Lindane	2.5×10^{-2}	2.1 - 3.3	Collards, Alfalfa
Methoxychlor	4.7×10^{-3}	1.8 - 6.3	Collards, Cherry
Toxaphene	1.9×10^{-3}	1.6 - 15.1 (25.2)**	Collards, Grass, Kale, Cotton, Alfalfa, Trefoil
Diazinon	8.0×10^{-3}	0.4 - 5.3	Com, Tomato, Cotton Endive, Kale, Wheat
Carbaryl	3.4×10^{-3}	1.2 - 7.4 (25.4)**	Cotton, Lima Beans, Tomato, Strawberry
Carbofuran	3.1×10^{-2}	1.1 - 8.1	Cotton, Strawberry, Alfalfa. Citrus
Captan	3.8×10^{-2}	9.0	Strawberry
2,4-D	27.8	1.1 - 8.8	Grasses

* Typical values in temperature range 20 - 30°C
** Maximum in brackets and next highest value

TABLE 8.2.3

Season of Application and Depth

	Depth - cm.				Fraction Applied			
	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
2,4-D	1	1	1	1	(0.2)	0.4(0.4)	0.4(0.2)	0.2(0.2)
MCPA		1	1	1		0.4	0.4	0.2
Alachlor	10/1	10/1	10/1		(0.2)	0.8(0.6)	0.2(0.2)	
Atrizine	10/1	10/1	10/1	10/1	(0.2)	0.8(0.5)	0.1(0.2)	0.1(0.1)
Butylate		10				1.0		
Cyanazine	10/1	10/1	10/1		(0.2)	0.8(0.6)	0.2(0.2)	
Linuron		1	1			0.5	0.5	
Metolachlor	10/1	10/1	10/1		(0.2)	0.7(0.5)	0.3(0.3)	
Metribuzin		10/1	10/1			0.5	0.5	
Trifluralin	10	10			(0.5)	1.0(0.5)		
Aldrin								
Carbaryl	1	1	1	1	(0.2)	0.2(0.2)	0.7(0.5)	0.1(0.1)
Carbofuran	10/1	10/1	10/1		(0.3)	0.9(0.6)	0.1(0.1)	
Chlordane		10	10				1.0	
Dieldrin								
Diazinon	1	1	1	1	(0.1)	0.2(0.2)	0.7(0.6)	0.1(0.1)
Endosulfan		1	1	1		0.2	0.7	0.1
Endrin								
Lindane		10				1.0		
Methoxychlor		1	1			0.2	0.7	0.1
Mirex								
DDT								
Toxaphene								
Captan		1	1	1		0.2	0.7	0.1
Chloropicrin				10				1.0
Dichloropropanes				10				1.0
Dichloropropenes				10				1.0
Methylisothiocyanate		10				1.0		

1 indicates surface application to 1 centimeter depth
10 indicates soil incorporation to 10 centimeters
1/10 indicates both of the above application modes are used in the season
( ) fractions in brackets are used in the southern states of Texas, Louisiana, Mississippi and Florida

TABLE 8.2.4

Comparison of Estimated Provincial Total Pesticide Use with Non-Confidential (1985) Sales Volumes

Pesticide	Ontario 1985 Sales 10^3 kg	Ontario 1983 OMAF 10^3 kg	Ratio	Quebec 1985 Sales 10^3 kg	Quebec 1982 Present Estimate 10^3 kg	Ratio	Atlantic 1985 Sales 10^3 kg	Atlantic 1984/86 Present Estimate 10^3 kg	Ratio
Herbicides									
2,3-D/DB/DP	527	264***	0.50	86	100	1.17	26	7	0.25
MCPA	131	157	1.20	79	66	0.83	41	12	0.30
Atrazine	1903	1730	0.91	727	454	0.63	17	17	1.02
Trifluralin	54	79	1.47	9.9	10.4	1.05	-	-	-
Insecticides									
Carbaryl	-	-	-	11.5	17.2	1.50	5.3	1.9	0.36
Chlordane	25	1*	0.04	17.0	0.24	0.01	2.0	0.27	0.13
Diazinon	51	14	0.27	12.6	5.9	0.47	4.3	2.6	0.61
Lindane	9.2	0.11**	0.01	3.3	0.03	0.01	0.20	0.002	0.01
Methoxychlor	3.7	2.6	0.69	0.6	0.6	1.00****	0.10	0	0
Fungicides									
Captan	-	-	-	72	57	0.79	-	-	-

* Chlordane used for termine control not included
** Lindane used for seed treatment not included
*** Includes roadside spraying
**** Methoxychlor estimate matched to sales to permit other organochlor estimates

( ) fractions in brackets are

Figure 8.2.1

Estimated 1975 Monthly Evaporation from Soil at Toronto International Airport Total Observed Precipitation and Rain are also Shown

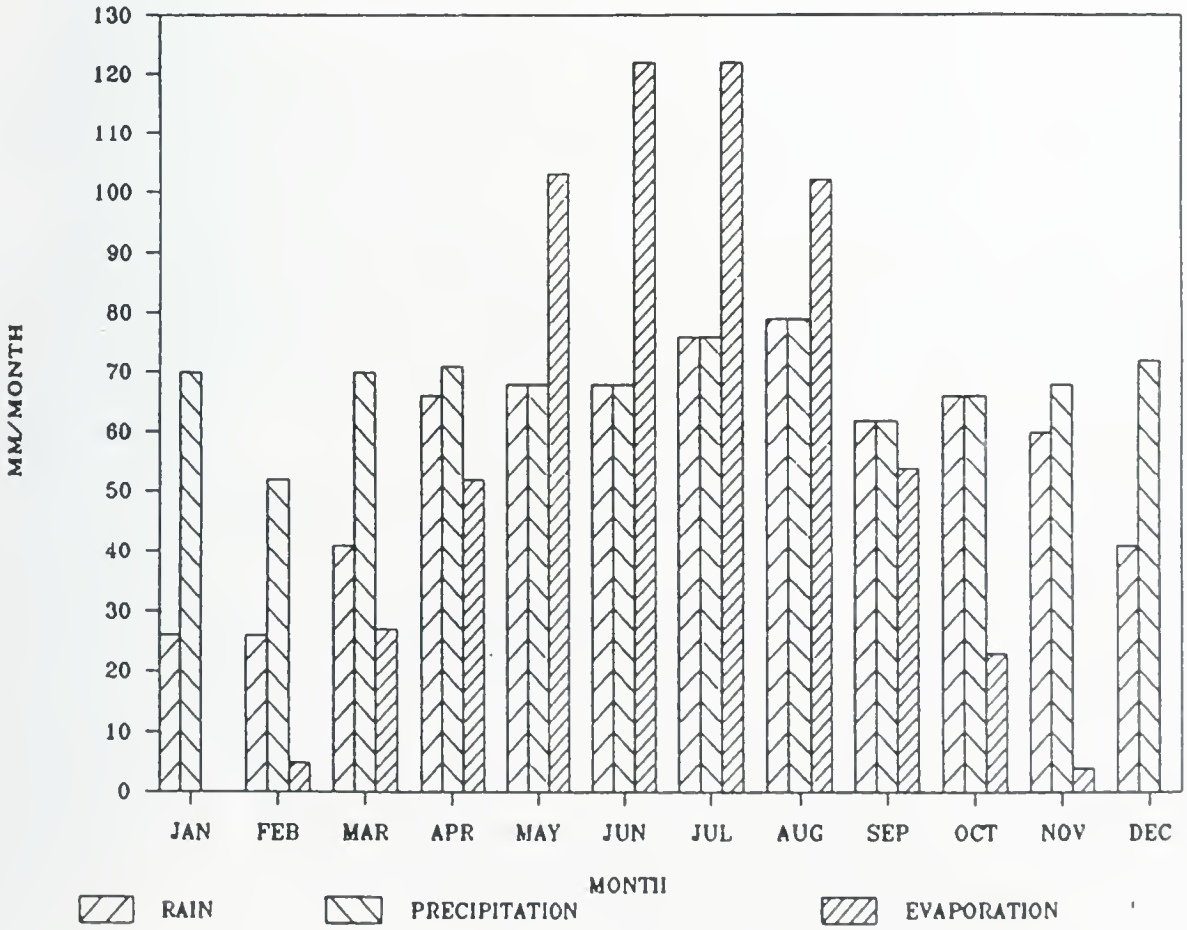


Figure 8.2.2
Emission Factors from Soil for Alochlor Incorporated to a Depth of 1 cm (E=Net Evaporation in mm/d; D=Net Soil Drainage in mm/d)

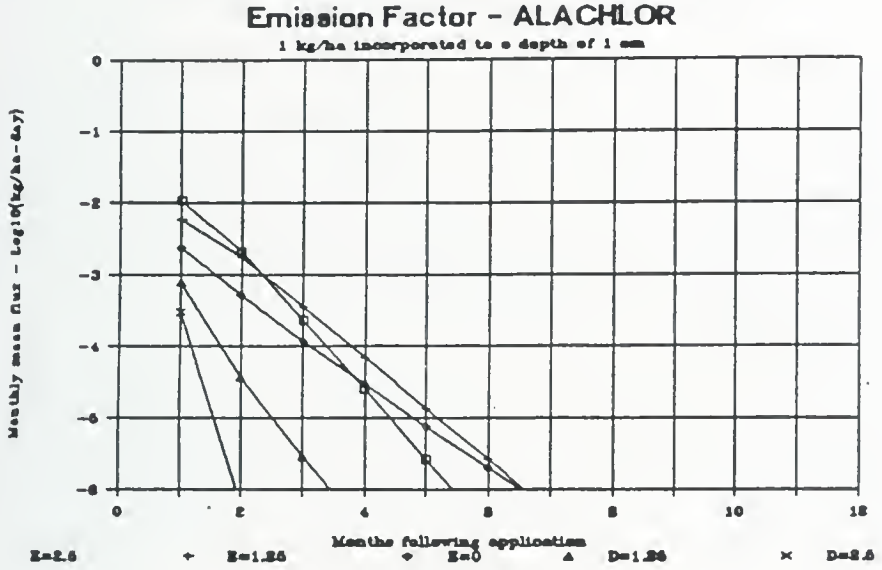


Figure 8.2.3
Emission Factors from Soil for Atrazine Incorporated to a Depth of 1 cm (E=Net Evaporation in mm/d; D=Net Soil Drainage in mm/d)

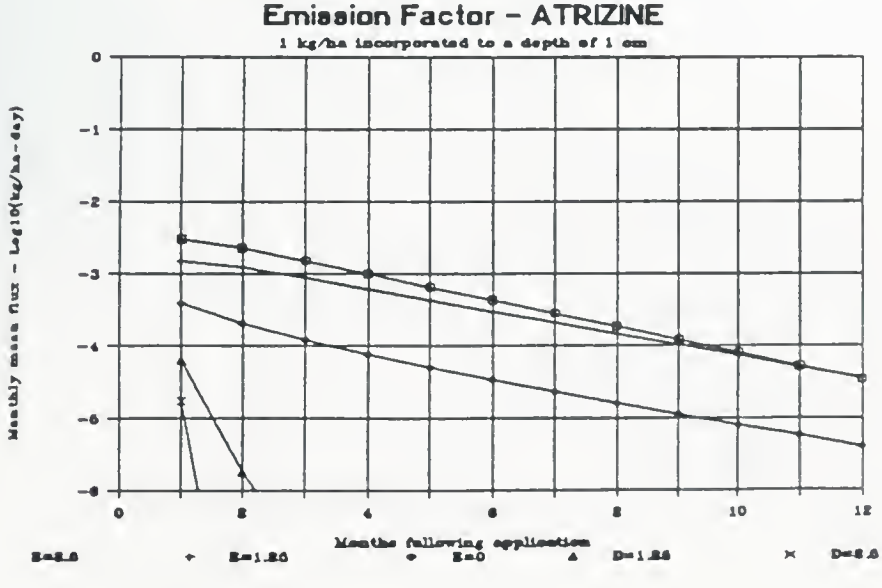


Figure 8.2.4
Emission Factors from Soil for Methoxychlor
Incorporated to a Depth of 1 cm (E=Net Evapo
ration in mm/day; D=Net Soil Drainage in mm/day)

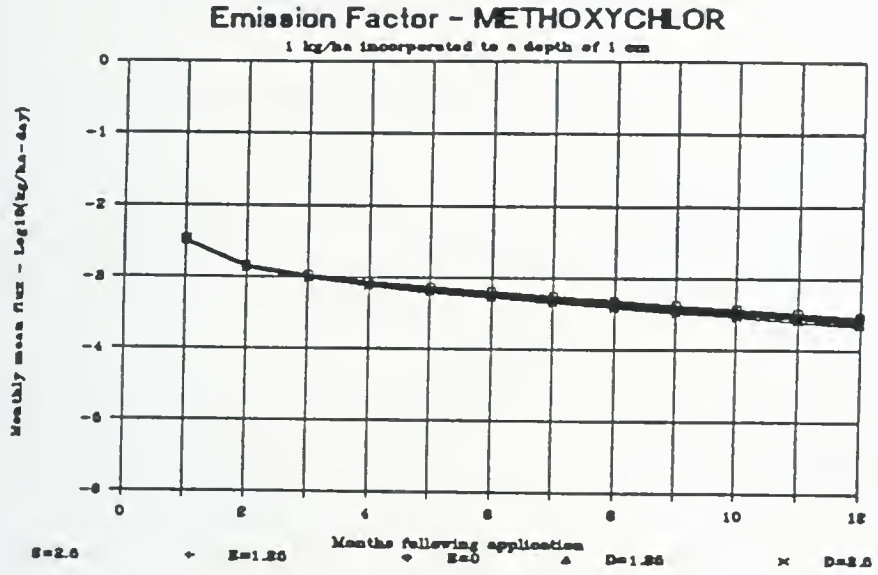


Figure 8.2.5
Emission Factors from Soil for Carbofuran
Incorporated to a Depth of 1 cm (E=Net Evapo-
ration in mm/day; D=Net Soil Draining in mm/day)

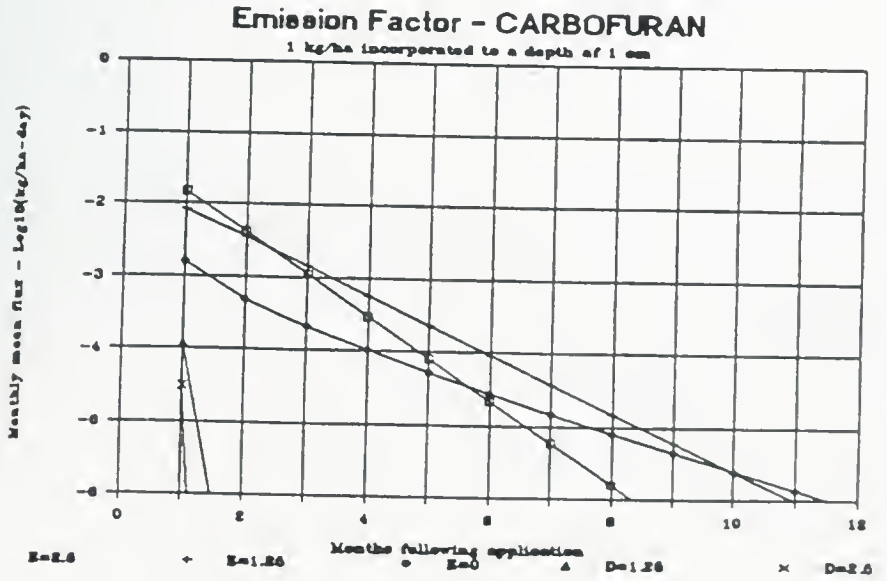
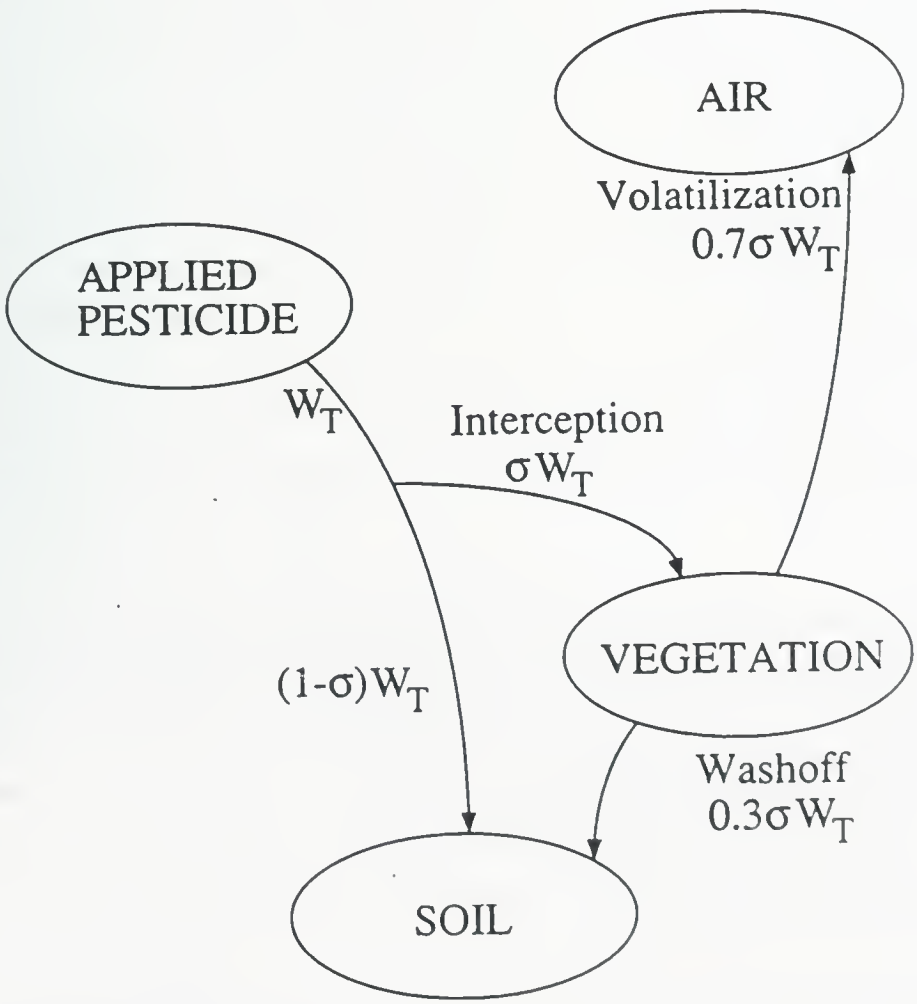


Figure 8.2.6

Pathways of Pesticide Emission to the Atmosphere used to Derive Emission Factors for Agricultural Application
Vegetation Shading Factor = σ



8.3 Toxic Emissions from Landfills

From the emissions estimation viewpoint, these sources can be broadly classified into those which emit through passive diffusion of toxics to the surface and those where emissions are carried to the surface by gas evolved due to changing atmospheric pressure and in the processes of chemical degradation and decay. Examples of passive sites are the majority of modern toxic chemical waste dumps receiving mainly chemical, filter sludge and ash wastes: biological activity is minimal or inhibited. Sites which evolve gas include mainly sanitary landfill sites and those which receive or have previously received a mixture of industrial and municipal wastes such as the Love Canal dump site (Shen and Tofflemire 1980). While passive sites may contain vast quantities of toxic chemicals, the rates of diffusion and emission to the atmosphere are not necessarily excessive, although the presence of other volatile chemicals might mobilize some toxics. Gas evolution from a landfill, by way of contrast, can be an efficient vehicle for carrying volatile toxics to the surface, even though only trace amounts may be present in the highly permeable refuse. Shen and Tofflemire (1980) give a review of the processes of emission resulting from land disposal of toxic wastes.

Some air concentration profile and surface flux estimates are reported in the literature (for example Lewis et al 1985 (PCB), Bennett 1987 (organics)). However, as for other open source emissions these data are too few to provide a basis for emission estimates for the large number of chemical species to be considered in this study. An estimate of 2,3,7,8-T_4CDD emissions from a disposal site due to volatilization has been made as referenced by MOE (1985) and summarized by Voldner and Ellenton (1987).

Several factors and algorithms are reported for landfill emissions, with and without biogenic gas evolution (Shen and Tofflemire 1980, Shen 1981, Bilsky 1985, Bennett 1987 (review)). The most recent algorithms which

include diffusive and bulk gas transport processes, are given by Ehrenfeld and Ong (1984) and Engineering-Science Inc. (1986). These algorithms rely on estimates of the concentration of toxics present and the area of landfill.

Establishing the actual toxics present in landfills and chemical waste dumps is problematic, particularly for older sites before proper records were kept (MOE 1985). Where sites contain incinerator or power plant ash, a reasonable estimate of the dioxin content of the ash is available (MOE 1985). Some information exists for the major chemical waste dumps particularly in the Great Lakes area (Hallett 1985). Tosine et al (1985) report concentrations of PCB, dioxins, dibenzofurans and other chlorinated organics in municipal refuse. Very limited data are available on unspeciated PAH in waste sites (Engineering-Science Inc. 1986).

For those chemical species which are known to be present in the landfill, the gas phase concentrations of the toxics in the refuse below the capping soil must be estimated in order to apply the algorithms. These concentrations can be estimated assuming saturation vapour pressure of the toxic in the gas phase (Bennett 1987), or the estimate could be based on the partition relationships for the solute/water/air/solid system, using a concentration estimate in one phase and assuming an equilibrium distribution between phases in the refuse. For the trace toxics considered in this study, vapour saturation would be most unlikely, especially since partitioning between the phases in the fill invariably favours the solid phase. If concentration data for either the gas or solid phase are available, then these can be used directly. This is the method used to estimate PCB and dioxin emissions from sanitary landfills. There are insufficient available data to estimate air emissions from chemical waste dumps most of which are inactive and do not emit gas.

The assumptions made in deriving the emission algorithms for open and closed landfills are generally more appropriate for more volatile materials

than are being considered here. The adsorption of the volatile material in the soil cap is neglected in these algorithms, whereas the adsorption on soil of trace toxics with low volatility is an important containment process for toxics such as dioxins and PCBs, making them relatively unavailable for gas phase diffusion. All the algorithms require detailed data such as the concentration of the toxic in the fill material; such data are not generally available.

For landfills which evolve methane due to biological activity, a direct estimate of the emissions associated with the gas evolution can be made where data on the concentrations of the toxic in the gas are available. This estimation method has been applied for PCDD and PCB emissions from sanitary landfills.

8.3.1 PCB and Dioxins from Sanitary Landfills

The major route for emission of these toxics from landfills is as a volatile component of evolved gas. Landfill gas is mainly methane and carbon dioxide and is produced by the biodegradation of refuse (U.S. EPA 1988a). The estimation of emissions due to gas evolution requires an estimate of the concentration of the toxic in the gas and the gas production. Murphy et al (1985) report the concentration of methane and PCB in sanitary landfill vent gases. The mean PCB concentration was 190 ng/m^3 of total gas which comprised approximately 50 percent methane. Based on an estimated range of 6 x 10^{10} to 24 x 10^{10} m^3/year methane production in the U.S., PCB emissions from this source are estimated by Murphy et al to be in the range of 10 to 100 kg/year. The higher estimate of 100 kg/year has been used in the present inventory.

Tosine et al (1985) report measured concentrations of PCDD, PCDF and PCB in six samples of municipal refuse supplied to two Ontario incinerators. The analyses speciated the PCDD/PCDF emissions into the tetra to

octachlorinated range of congeners. PCDF were detected in only one sample. The PCB and dioxin data have been averaged over the six tests to provide the following means on which emission estimates for this study are based:

Congener	Mean Concentration	Range
T_4CDD	0.25 ng/g	n.d. - 1.5 ng/g
P_5CDD	0.45	n.d. - 2.7
H_6CDD	8.0	n.d. - 26
H_7CDD	27	2 - 87
O_8CDD	74	7 - 330
Total	110 ng/g	10 - 440
PCB	360 ng/g	110 - 1500

Using estimates of the partition coefficients for air/water/organic carbon, the gas concentration of 190 ng/m^3 found by Murphy et al yields an estimated range of concentrations of PCB in the refuse of 0.2 to 2.5 mg/kg. This is in good agreement with the 0.11 to 1.5 mg/kg reported by Tosine et al in the above table, lending some degree of confidence in the calculation method used here.

Based on the same methods, the reverse computation can be carried out to infer the concentrations of the PCDD congeners in the landfill gas based on their concentrations in the refuse. While this method can yield no more than a gross estimate of the emissions, it is a worthwhile exercise to provide some estimate of the importance of landfill sites as sources of PCDD.

Assuming equilibrium, the concentration of a volatile in the gas phase, C_g, can be written in terms of the concentration in the landfill solids, C_s, and the partition coefficients K_h and K_{oc} for air/water and solids/water, respectively, as:

$$C_g = C_s \ (K_h/K_{oc})/f_{oc}$$

where f_{oc} is the fraction of organic carbon taken to be 0.1. The partition coefficients typical of each degree of chlorination were estimated using Rordorf 1989, Friesen et al 1985 and Webster et al 1985. Using a total gas evolution of 4.8×10^{11} m^3/year, the following total U.S. emissions from landfills are estimated, assuming that landfill gas is vented to the atmosphere without combustion or other control:

T_4CDD	25	pg/m^3	12	mg/year
P_5CDD	3.4		1.6	
H_6CDD	8.0		3.8	
H_7CDD	8.0		3.8	
OCDD	4.0		1.9	
Total PCDD			23	mg/year
Total PCB			100	kg/year

The U.S. population in 1987 was 277 million. The dioxin and PCB emission estimates for the U.S. were reduced to per capita emission factors which were then applied to the population distributions in both Canada and the U.S. gridded areas.

8.4 Chemical Spills and Chemical Waste Disposal Sites

The sources of emission in this category include:

- accidental spills from mobile tankage due to rupture or major leak loss
- deliberate spraying of unpaved roads with contaminated oil to suppress dust (Frank et al 1981)
- spills and leakage at toxic waste storage sites and electrical equipment storage areas (e.g., transformers)

Accidental spills can be further categorized into fresh-spill emissions in the 1985 base year and residual volatilization and dust emissions from prior year spill-sites.

Fresh-spill emissions, while the toxic is present on the surface in macro quantities, can be estimated on the basis of extent, soil temperature, vapour pressure and typical aerodynamic resistance. The event-scenario will be different for each individual spill and the emission should be estimated on a case-specific basis. Information on 1985 spills are available from Provincial environmental authorities. Similarly, Voldner and Ellenton (1987) have summarized PCB spill data in Great Lakes States that have been reported during 1983 and 1984 in other studies. In view of the high priority given to spill clean-up and removal after a spill of this nature, air emissions are likely small compared to other open sources such as transformer storage.

PCB contaminated waste oil, previously used as a dust suppressant, is also unlikely to be an important primary source of emission. Road material is typically low in organic content and the downward leaching in such soil is more rapid than those with high humus content. No quantitative data have

been located which would permit a meaningful estimate of emission from this open source. Similarly, for emissions from toxic waste storage, while the location of waste storage sites can be determined from Permit Records, in the absence of compound specific emission factors or the details of minor spill events, meaningful emission estimates can not generally be made (MOE 1985). In the case of PCB emissions from in-service and stored transformers and capacitors, it is possible to make a first order estimate based on published data.

8.4.1 PCB from Transformers and Capacitors

The Canadian Council of Resource and Environment Ministers (1988) has compiled a Canada-wide inventory of PCB waste storage sites. The inventory was compiled by categorizing waste liquids into those with less than 500 ppm, termed 'low concentration' waste. The total litres or kilograms of liquid are reported, but not the actual amounts of PCB. In Ontario, this inventory subdivides sites into 'major sites' containing more than 1 tonne of waste liquid and 'minor sites' with less than 1 tonne. For some of the major sites, the tonnes in storage are reported, but the information is not sufficiently complete to permit a meaningful estimate of total stored quantities.

An appendix to documents prepared for hearings on proposals for the regulation of mobile PCB destruction facilities in Ontario, provides a compilation of the main locations and quantities of both in-service PCB and stored waste for Ontario as of May 1984. This document has been used as the basis for an estimate of PCB emissions for Ontario for combined in-service and waste PCB. Emissions for the other Canadian provinces have been estimated due to using a per capita emission factor.

An emission factor for leakage and spillage of PCB can be derived from Alliance Technologies (1987) based on their estimate of leakage/spillage of PCB from utility industry closed systems equipment in the United States.

The following data are extracted from their report:

Type of Equipment	Total PCB (lbs)	Leaked/Spilled (lbs/year)
Transformers (Askarel)	74 597 283	20 448
Large capacitors	87 552 960	369 251

If one assumes a similar mix of transformers and capacitors in Ontario, then an annual leakage/spillage rate of 0.0024 lbs PCB per pound of PCB is estimated. It is pointed out in the Alliance report that there is as yet no method for estimating atmospheric emissions which result from spills, and it is suggested that a rough estimate may be made using 4.3 g/L which is based on uncovered dredge spoils. Using a mean density of 1400 kg/m^3 for PCB, and assuming that spilled PCB emits for a year before clean-up or other removal process, an emission factor of 7.2 mg per kilogram of total PCB in transformers and capacitors is estimated.

The Alliance (1987) report estimates an annual leakage/spillage of 503680 lbs of PCB. Using the above emission factor, an annual emission of 530 kg of PCB is estimated to be emitted to the atmosphere from this source in the United States. Since 70% of the total U.S. population is in the gridded area of this inventory, 70% of the total, i.e., 370 kg of PCB, was assumed to be released within this area.

The data on which an estimate of the Ontario emissions is based is given in Table 8.4.1. For purposes of the emission estimate, it is assumed that 65% of the high level PCB liquid in-service or storage is PCB of specific gravity 1400 kg/m^3. Low concentration waste with less than 500 ppm PCB was not included in the estimate. Table 8.4.1 shows a total annual PCB emission from in-service and waste PCB of 33.6 kg. The results in Table 8.4.1 were allocated to the UTM grid by city location or by area apportionment where only county or regional totals are available. The U.S. total estimate has

been gridded by population. For other Canadian provinces, the U.S. per capita emission factor is applied to population to provide a gridded emissions estimate.

8.4.2 Dioxins from Trichlorphenol Sites

The production and use of 2,4,5-trichlorphenol (2,4,5-TCP) and the disposal of its production wastes constitute what are likely the largest localized sources of 2,3,7,8 tetrachloro-dibenzo-para-dioxin (2,3,7,8-TCDD). The U.S. EPA has published a National Dioxin Study in a Report to Congress (U.S. EPA 1987g) which lists sites which have been contaminated either during production or through waste disposal and spills. These sites are classified as follows:

Tier 1:	Production sites
Tier 1A:	Waste disposal sites associated with production
Tier 2:	Use sites for pesticide manufacture
Tier 2A:	Waste disposal sites associated with use

Table 8.4.2 has been extracted from the National Dioxin Study Report. The tables in the original document include other information and should be referenced to properly interpret the data provided here. The table gives some idea of the ranges of 2,3,7,8-TCDD concentrations which have been detected in soil samples at the Tier 1 and 2 sites. While the number of samples is given in some cases together with the minimum and maximum concentrations found, it is not possible on the basis of available data to estimate either an average soil concentration or an affected area for the site which would provide some basis for an emission rate estimate using the Jury et al (1983) model. Furthermore, the data reported have been used in part for setting priorities for remedial action. For many sites in 1987, remedial action was already in progress or complete. Hence, the majority of the significant concentrations reported are no longer current for purposes of emissions estimation.

While emissions of 2,3,7,8-TCDD and other contaminants from these sites cannot presently be estimated, an emission factor based on the Jury model can be derived based on Eduljee (1987). Most of the sites are greater than ten years old and the emission factor is estimated to be of the order of 0.5 milligrams/(ha-year) per ppb 2,3,7,8-TCDD concentration in the surface soil.

TABLE 8.4.1

In-Service and Waste Storage PCB Inventory

Location or Municipality	High Level PCB		Total PCB	Annual Emission
	In-Service litre	Waste litre	kg*	kg
Bruce Township	178000	12000	163000	1.17
Oshawa	35000		31900	0.23
Ajax	1400		1300	0.01
Pickering	33000		30000	0.22
Whitby	1600		1500	0.01
Other in Durham	2500		2300	0.02
Burlington	14200		12900	0.09
Oakville	82000	26000	98300	0.71
Halton Hills/Milton	7300		6600	0.05
Hamilton Wentworth	860000	28000	808000	5.82
Dundas/Stoney Creek	9000		8200	0.06
City of Nanticoke	226000	1200	206000	1.49
Other Haldimand/Norfolk	11400		10400	0.07
London	104000	750	95300	0.69
St. Thomas }				
Woodstock }				
Aylmer }	74600	1000	68800	0.50
Tillsonburg }				
St. Mary's }				
Niagara Falls	9000		8200	0.06
St. Catharines	80000		72800	0.52
Thorold	59000		53700	0.39
Welland	121000	4000	113000	0.82
West Lincoln Twp.	-	180000	164000	1.18
Ottawa-Carlton Region	270000	3200	249000	1.79
Mississauga	136000	3000	126000	0.91
Brampton	33000	500	30500	0.22
Peterborough	110000	25000	123000	0.88
Sault Ste. Marie	420000	3100	385000	2.77
Sudbury	349000	36000	350000	2.52

TABLE 8.4.1 (Contd.)

In-Service and Waste Storage PCB Inventory

Location or Municipality	High Level PCB		Total PCB	Annual Emission
	In-Service litre	Waste litre	kg*	kg
Capreol Nickel Centre Onaping Falls	94000	2600	87900	0.63
Thunder Bay	161000	10000	156000	1.12
City of Toronto	591500	30000	566000	4.07
City of North York	39000		35500	0.26
City of Etobicoke	78000	36000	104000	0.75
City of Scarborough	36000		32800	0.24
Borough of York	16000		14600	0.10
Borough of East York	31000	-	28200	0.20
Metro Toronto and unassigned industrial	97000	3500	91500	0.66
Cambridge	11700	2500	12900	0.09
Kitchener	95700	8000	94400	0.68
Waterloo	19000	3000	20000	0.14
Windsor	165500	22000	171000	1.23
Amherstburg Essex Harrow Leamington Chatham	31000	1300	29400	0.21
TOTAL:				33.58

* Assuming 65% PCB of specific gravity 1.4 in liquid

TABLE 8.4.2
Tier 4 Dioxin Sites

Name	State	Tier	Number of Samples	Soil Concentration Min. ppb	Max. ppb
Diamond Alkali	NJ	1	9	60	51000
Hooker Chem. Buffalo Ave.	NY	1	17		18600
Dow Chemical Co.	MI	1	106		1500
Syntex Agribusiness	MO	1	74		979
Hooker Chem. Buffalo Ave.	NY	1	5	5	524
Dow Chemical Co.	MI	1	43	0.04	52
Baird and McGuire	MA	1	96		48
Chemical Insecticide	NJ	1	61	0.09	17
Baird and McGuire	MA	1	18		11
Givauden	NJ	1	37		10
Olin Chemical Corp.	NY	1	15		9
Brady Metals	NJ	1A	10	2	3500
Brady Metals	NJ	1A	14	1	1900
Hooker Chem. Love Canal	NY	1A	?		7
Hooker Chem. 102nd St.	NY	1A	10		0.6
Hooker Chem. 102nd St.	NY	1A	14	173	630
Arkansas Best Freight	MO	1A	25		6
Baldwin Park	MO	1A	67		743
Baxter Garden Center	MO	1A	19		82
Russell Bliss Farm Rd.	MO	1A	7		382
Bliss Property	MO	1A	74		120
Bonifield Bros. Trucking	MO	1A	5	13	56
Bubbling Springs Arena	MO	1A	11		95
Bull Moose Tube Co.	MO	1A	106		29
Cashel Residence	MO	1A	82		250
Community Christian Church	MO	1A	134		230
Community Christian Church	MO	1A	2		0
East North Street	MO	1A	107		6
East Texas Motor Freight	MO	1A	71		52
S.B. Erwin Farm	MO	1A	20		3
Erxleben Property	MO	1A	129		280
Hamill Transfer Co.	MO	1A	145		155
Jones Tuck Lines	MO	1A	5	8	22
Lacy Manor Development	MO	1A	102		48

TABLE 8.4.2(Contd.)

Tier 4 Dioxin Sites

Name	State	Tier	Number of Samples	Soil Concentration Min. ppb	Soil Concentration Max. ppb
Manchester United Church	MO	1A	121		5
Minker Residence	MO	1A	289		340
Neosho Digester	MO	1A	10		<1
Neosho Tank Water	MO	1A	41		32
Overnite Transport Co.	MO	1A	180		17
Piazza Road	MO	1A	360		1800
Piazza Road	MO	1A	105		1020
Quail Run Mobile Home Pk.	MO	1A	341		1650
Romain Creek	MO	1A	251		272
Robert Rusha Farm	MO	1A	8		5
Saddle and Spur Riding Cl	MO	1A	91		31
Shenandoah Stables	MO	1A	19		1750
Sontag Road	MO	1A	765		588
Southern Cross Lumber	MO	1A	11		27
Stout Residence	MO	1A	374		241
Sullins Residence	MO	1A	57		820
Royal Valley Farm	MO	1A	15		16
Timberline Stables	MO	1A	24		42
Times Beach	MO	1A	451		1200
Monsanto	WV	2	400		400
Superior Solv. and Chem.	MO	2	48		160
Amchem	PA	2	9		118
Thompson-Hayward Chem. Co.	KS	2	46		46
Artel Chemicals	WV	2	189		19
Monsanto Queeny Plant	MO	2	3		
Eastman Kodak	NY	2	23		
Manila Creek	WV	2A	19		57
Conservation Chem. Co.	MO	2A	61		29
Poca Landfill	WV	2A	9		18
Nitro Dump	WV	2A	6		2
Heizer Creek	WV	2A	19		1
Alkali Lake	OR	2A	40	0.01	0.06

8.5 Forest Fires

8.5.1 Description

Forest wildfires can be strong sources of PAH emissions because combustion is usually inefficient and incomplete (U.S. EPA 1987a). For example, the Ontario Ministry of the Environment estimated that forest fires and slash burning were the most important sources of atmospheric PAH in Ontario during 1976 (MOE 1979). However, large recorded differences in the number of fires and areas of burning occur each year. The size and intensity of a wildfire with resulting air pollutant emissions are hypothesized to depend on variables such as: meteorological conditions, the species, moisture content and age of vegetation burned, topographical features such as land slopes, and the available consumable fuel in the burn area (U.S. EPA 1988b). It has been reported that the most important fuel characteristics that affect PAH emissions are fuel loading and moisture content (U.S. EPA 1987a). Controlled or prescribed fires have provided some information pertinent to wildfires. Of the various techniques used in prescribed burning, heading fires (that spread in the direction of the wind) are expected to often result in the lowest combustion efficiency whereby many fuel elements are not burned completely in the active fire zone (i.e. large areas of smoldering) (U.S. EPA 1987a). Because forest fires may spread in any direction, both heading and backing fire conditions may occur at different times. Similarly, since reliable emission measurements have not been conducted at sites of actual wildfires, large uncertainties can be expected in any estimates of forest fire emissions.

8.5.2 Emission Factors

Laboratory measurements of PAH from pine needle burning have been done under simulated backing and heading fire conditions at various fuel loading rates (0.5 - 2.4 kg fuel/m^2) and for both flaming and smoldering conditions (U.S. EPA 1987a). The range of reported emission factors is shown in Table 8.5.1 and represent particulate PAH only. A large variation between burning conditions was evident and the degree to which these represent actual emission rates is uncertain. Average PAH emission factors from other laboratory assessments on different species are also tabulated in which information on burn conditions was not provided (Versar 1989). In most instances, the average factors were within the range shown for comparable species. In order to select and apply emission factors for all measured PAH components, the reported average factors (Versar 1989) were used directly for some species and median emission factors for 2.4 kg/m^2 burn conditions (U.S. EPA 1987a) were used for the remaining species. This fuel loading rate is equivalent to loadings reported for north central and eastern forest regions (U.S. EPA 1988b). It should be noted that the total PAH emission factor derived is of similar magnitude to that of residential wood burning in fireplaces (see Section 5.6). Furthermore, it is noteworthy that B(a)P was not detected in a set of slash burn smoke extracts possibly due to transformation of this somewhat reactive species under conditions of the burn (Standley and Simoneit 1987). Total PAH was found to comprise less than 0.3 - 2.4% of the total extractable organic matter in the aerosols of these studies. On the other hand, benzo(a) pyrene has been detected in other prescribed burn smoke samples (White 1985) and has been used as a specific indicator of forest fire impacts (Morales et al 1979).

No direct emission test information was found with which to derive emission factors for other toxic chemical components in wildfire emissions such as dioxins. However, such toxic constituents might be expected, especially upon burning pesticide-treated forest lands. Accordingly, forest fire PCDD

emission estimates based on surrogate data (i.e. residential wood combustion particulate), have been made (Sheffield 1985). These data were based on PCDD content in woodstove chimney particulate material. Since PAH emission factors applied to forest fires were found to more closely resemble fireplace emission factors than woodstoves, available data for fireplace emissions were used. Only one measurement of fireplace chimney particulate PCDD and PCDF content was found (Clement et al 1985) and the product of these data and the average total particulate emission factor for forest fires (U.S. EPA 1988b) was used to derive emission factors for these components. The resulting estimated particle phase emission factors are shown in Table 8.5.2 and large uncertainties are associated with these.

8.5.3 Inventory Comments

On average, it can be expected that forest fire contributions to air quality in some areas can be significant during the growing seasons. However, due to the highly variable nature of such fires (i.e., both extent and type of fuel burned) the significance or emission impact is also expected to be highly variable. For example, on the basis of fire records, Ontario experienced the lowest burn area during 1985 than most other years. Thus, the contribution by wildfires for this base year was abnormally low. In determining forest fire emissions, the average mass of fuel burned in wildfires is estimated to be 22 tonnes per hectare in Canada (Environment Canada 1978). In the U.S., the wildfire fuel consumption is estimated to vary between 20 to 135 tonnes fuel consumed per hectare for various regions of the country (U.S. EPA 1988b). The average fuel consumption is 20-25 tonnes/hectare in the southern, north central and eastern regions which are most applicable to this inventory.

TABLE 8.5.1

Particulate PAH Emission Factors Derived for Forest Fire Emissions (mg/tonne forest fuel consumed)

Constituent Emission	Emission Factor Range[1]	Reported Emission Factors[2]	Selected Factors
Total PAH	7,632-171,750	-	33,350
Anthracene	-	2,500	2,500
Anthracene/Phenanthrene	584-12,181	-	-
Benz(a)anthracene	-	3,100	3,100
B(a)A/Chrysene	543-28,724	-	-
Benzofluoranthenes	129-12,835	-	2,600
Benzo(a)fluoranthene	-	1,300	-
Benzo(k)fluoranthene	-	1,300	-
Benzo(ghi)perylene	419-6,181	2,500	2,500
Benzo(a)pyrene	33-3,454	740	740
Benzo(e)pyrene	61-5,836	-	420
Chrysene	-	3,100	3,100
Fluoranthene	687-14,563	5,500	5,500
Indeno(1,2,3 cd)pyrene	169-4,282	1,700	1,700
Methylanthracenes	449-9,400	-	4,000
Phenanthrene	-	2,500	2,500
Perylene	24-2,128	-	90
Pyrene	979-20,407	4,600	4,600

Notes:

1. Based on measurements for simulated open (backing and heading) fires of pine needles at burn rates of 0.5-2.4 kg/m^2 fuel loading (U.S. EPA 1987a).

2. Average emission factors for simulated open burning (Versar 1989).

TABLE 8.5.2

Particulate PCDD and PCDF Emission Factors Derived for Forest Fire Emissions

Constituent	Particulate Content (µg/Kg)[1]	Estimated Emission Factor (mg/tonne forest fuel consumed)[2]
Total PCDD	3.1	0.026
T_4CDD	ND	0
P_5CDD	0.5	0.0043
H_6CDD	1.7	0.014
H_7CDD	0.5	0.0043
OCDD	0.4	0.0034
Total PCDF	3.9	0.033
T_4CDF	0.3	0.0026
P_5CDF	1.4	0.012
H_6CDF	1.7	0.014
H_7CDF	0.4	0.0034
OCDF	0.1	0.0009

Notes:

1. Based on constituent content in a fireplace chimney soot sample (Clement et al 1985)

2. Based on the product of the constituent content and the average total particulate emission factor of 8.5 kg particulate emission per tonne fuel consumed in forest fires (U.S. EPA 1988b).

8.6 Slash Burning

8.6.1 Description

Slash or prescribed burning is a controlled land management treatment used to reduce logging residues, manage forest production and minimize potential for destructive wildfires (U.S. EPA 1988b). Ignition or firing methods such as heading, backing, spot and flank fires are used to control fire behaviour patterns that depend mainly on the type and moisture of fuel to be burned and weather/wind conditions. Of the combustion phases that occur (i.e. preheating, flaming, glowing and smoldering), the smoldering phase produces greater amounts of incomplete combustion products per fuel quantity consumed than other phases. Control can be administered in this latter stage by rapidly extinguishing fires when lower layers of the fuel are moist. Emission factors of the combustion product mix have been predicted and are known to vary by as much as 50% with fuel and fire conditions. Agricultural burning is practiced routinely in major agricultural areas to clear or prepare land for planting and also to reduce the need for pesticides and herbicides (U.S. EPA 1987a, U.S. EPA 1988b, Versar 1989).

8.6.2 Emission Factors

As noted in Section 8.5, only laboratory data are available with which to derive emission factors of toxic chemicals for prescribed burning and are shown in Tables 8.5.1 and 8.5.2.

8.6.3 Inventory Comments

In the U.S. and Canada, estimates of the amount of available fuel consumed in regions by prescribed fires have been made. In some cases, these data are based on general locations and vegetation types burned for a given region. However, these estimates may not reflect actual prescribed burning

activities in a specific region. Statistics on the extent of prescribed burning in Ontario have been compiled by the Ministry of Natural Resources which were used in the current inventory (MNR 1986). These statistics were considerably lower than previously estimated data and no estimates are available for agricultural burning. Hence, emissions calculated for this sector are regarded as being highly uncertain.

8.7 Miscellaneous Opening Burning

8.7.1 Description

There are numerous types of open burning activities or incidents that can be expected to contribute emissions of toxic chemicals to the atmosphere. On the other hand, very few estimates of emissions from such occurrences have been reported. Fires may be small such as in cases where periodic burning is used to reduce waste volumes and facilitate waste disposal. In some other cases, fires may not be deliberate and can result in either small or large impacts. Examples of miscellaneous open fires are:

- transformer or capacitor fires,
- structural fires,
- burning of used railway ties,
- intentional or accidental automotive burning (e.g. auto bodies, tires or other components),
- burning of landscape refuse (e.g. grass clippings, leaves and branches),
- municipal refuse burning (e.g. general or domestic trash).

There is concern that accidental releases of PCBs, PCDDs and PCDFs might result during infrequent occurrences of PCB-containing transformer fires (Sheffield 1985). For example, these contaminants have sometimes been detected in oily soot samples taken in areas where transformers or other electrical components have overheated or burned (Staiff et al 1972, Hutzinger et al 1985, Orris et al 1986, Fitzgerald et al 1986, Erickson et al 1985, des Rosiers and Lee 1986). No release of such compounds during normal operation has been reported. Specific preventative recommendations have been made by Environment Canada to minimize such fires (EPS 1985a). On the basis of wipe samples, contaminated soot

from such fire deposits quite locally and data suggest only limited dispersion of these contaminants following a fire. The quantity of contaminant release has not been estimated since such fires occur variably and infrequently, control measures are applied to the use of PCBs in electrical equipment and no atmospheric monitoring has been reported in conjunction with transformer fires (Sheffield 1985). Similarly, emissions of such contaminants from structural fires have not been estimated due to the variability and uncertainty of materials burned.

The burning of used railway ties, especially those preserved with PCP and creosote, might represent a significant source of PAH, PCDD and PCDF in some areas. For example, it has been estimated that if all chlorophenol-treated railway ties are burned, annual PCDD emissions in Canada would amount to approximately 6 kg (Sheffield 1985). In fact, an Environment Canada report indicates that many of the one million railroad ties disposed of each year in Canada is done by open field combustion (EPS 1985b). Emissions can be estimated using emission factors determined by Environment Canada based upon woodstove experimental testing. However, the extent of railway tie burning in Ontario is not known but is still practiced with permits in remote northwest regions of Ontario (CP Rail, personal communication 1990).

Other types of open fires such as burning of domestic or industrial/commercial refuse are expected to result in emissions of various contaminants. However, in most areas, open refuse burning is greatly restricted while municipal refuse and automotive burning is completely prohibited (U.S. EPA 1987a). Permits are often required for open burning of grass and leaves and this is prohibited in many municipalities, especially in urban areas.

8.7.2 Emission Factors

Emission factors of PCDD and PCDF for burning treated railway ties are shown in Table 8.7.1. These are based on Environment Canada's experimental burning and emission testing of unused, treated railway ties in a controlled air, horizontal baffle-type wood stove (EPS 1985b). Testing was done with open stove doors in order to simulate open burning as much as possible and results were considered by the investigators to be qualitative only.

Particulate and gaseous PAH emission factors for general and landscape refuse open burning are shown in Table 8.7.2. These are based upon emission measurements in laboratory open burning simulation tests in which major conditions such as fuel type, rate of burning and measurements could not be readily controlled outdoors (U.S. EPA 1987a).

8.7.3 Inventory Comments

As mentioned above, used railway tie burning is still practiced in Canada but the extent and locations are extremely uncertain. However, specific PCDD and PCDF emission estimates can be done using several assumptions. For example, if one million railway ties are burned per year in Canada, each weighing 50 kg and one-half are PCP-treated with the balance creosote-treated, application of the above emission factors indicates a total annual PCDD emission rate of 0.017 kg. PCDF emission rates are then expected to be lower. Similarly, if approximately 15% of these ties are burned in Ontario, the resulting estimated emissions are ~0.0026 kg PCDD. These estimates suggest a much smaller contribution by this source than another Canadian estimate (i.e. approx. 6 kg PCDD per year) which was done prior to the availability of emission test data (Sheffield 1985). Because of the base quantity uncertainties and unknown geographical apportionment, these emission estimates were not included in the inventory.

General open burning emissions have not been estimated for Canada since the extent of open burning (i.e. base quantities) is unavailable. Base quantities have been determined in the U.S. and the above-mentioned emission factors for PAH have been applied to both point and area sources comprising: municipal open burning dumps (SCC 501002), commercial/institutional and industrial open burning of wood refuse (SCC 502002 and 503002, respectively) and domestic, commercial and industrial open burning area sources. Assumptions were made on the predominant types of waste burned by these sources in order to apply the specific emission factor (e.g. municipal or landscape refuse burned). Similarly, the municipal refuse emission factor was applied to the area source base quantities in Ontario corresponding with open-pit municipal refuse burned.

TABLE 8.7.1

PCDD and PCDF Emission Factors for Burning Used Railway Ties Containing Preservatives (mg/tonne dry wood burned)[1].

Contaminant	PCP-Treated BC Fir	Creosote-Treated BC Fir
Total PCDD	0.243	0.448
T_4CDD	0.005	ND
P_5CDD	0.024	ND
H_6CDD	0.100	0.116
H_7CDD	0.063	0.242
OCDD	0.049	0.090
Total PCDF	0.233	ND
T_4CDF	0.028	ND
P_5CDF	0.014	ND
H_6CDF	0.077	ND
H_7CDF	0.068	ND
OCDF	0.047	ND

Note 1: Based on averages of triplicate emission tests done in a wood stove burning preserved railway ties under conditions to simulate open burning of used railway ties (EPS 1985b).

TABLE 8.7.2

PAH Emission Factors for Domestic, Commercial and Industrial Open Burning Sources of Refuse (mg/tonne refuse burned)[1].

Constituent	Open Burning Municipal Refuse	Open Burning Landscape Refuse
Total PAH	840	720
Anthracene	ND	ND
Benzo(ghi)perylene	30	30
Benzo(a)pyrene	70	70
Benzo(e)pyrene	50	30
Coronene	ND	ND
Fluoranthene	330	230
Perylene	ND	10
Phenanthrene	ND	ND
Pyrene	360	350

Note 1: Based on stack emission measurements in a laboratory combustor designed to simulate open burning in which both gaseous and particulate PAH compounds were collected (U.S. EPA 1987a).

9. DATABASE DESIGN AND IMPLEMENTATION

9.1 Overview of Computer Aspects

The toxic chemical emission inventory database has been developed for the base year 1985 and covers a region encompassing most of eastern North America. The domain includes all eastern provinces and Ontario but excludes some portions of northern Quebec, south-west Saskatchewan, most of Alberta and all of British Columbia, Yukon and North West Territories. In the US the inventory domain runs through northern Florida, and is bounded on the west by Texas, Oklahoma, Kansas, Nebraska, North Dakota and South Dakota. The spatial resolution used in Ontario is the variable sized UTM grid system (ORF/MEP 1983, EAG 1984) and is shown in Figure 3.7.2. The UTM/OME grid numbering system is presented on two maps, enclosed with this report. The first map shows all of Ontario with grid numbering, and the second shows an enlarged view of southern Ontario. Outside of Ontario an array of 33 by 33, 127 km grid squares on a polarstereographic projection (true at 60 N with a -10 degree polar rotation and an origin offset from the north pole of -7,239 km x-axis and -1,905 km y-axis) covering an area of approximately 4000 km square was used. Both grid systems are shown together in Figure 3.7.1.

Data files used in producing the toxics emission inventory were obtained from many different sources with highly variable contents and structures. Base quantity, activity level and temporal data for both point and area sources were received on:

- nine (9) track 6250 BPI ASCII tapes containing base quantity, temporal, and spatial data used in producing the 1985 NAPAP inventory from the US EPA,
- MS-DOS computer diskettes from OME and C & P (Environment Canada) containing base quantities and gridding surrogate files,

- literature and algorithm derived data for some sectors were manually entered as base quantities, or as annual emission values.

All emission factor data were manually entered and checked to ensure data quality. Although checks were performed during the processing of several data components, e.g. specific Canadian base quantities, quality assurance tests were not practical on much of the original data sets received for this inventory. However, most of these data were reported to receive extensive quality control during preparation of the NAPAP inventory (U.S. EPA 1989b).

9.2 Data Sources and Preparation

The process of reducing the incoming information to a common basis from which to develop the toxic, inventory utilized both mainframe and mini-computer environments. The ORTECH Vax/6310 was used to read in the ASCII foreign tapes supplied by the US EPA for use on this inventory. Before transferring the base quantity files (BQF), spatial allocation files (SAF), temporal factor files (TFF) and other related annual data files to the MS-DOS environment, the files were reduced in size by eliminating specific states, provinces and some source sectors that were not relevant to the inventory. This process was done on both point and area source files for Canadian and US sources. Other files used directly on the PC computer were: gridding surrogate data supplied by C&P, Ontario area source and point source gridded base quantities supplied by the MOE, Resources For the Future (RFF) state pesticide use data. The development of pesticide emissions is covered in Section 8 of this report. The raw incoming data from all sources were merged,and modified to assemble the three rudimentary files of the toxic chemical emissions inventory:

- BQF Point and Area base quantity, or activity level data files,
- EFF All sectors emission factor data files,
- TFF Point, Area and Pesticide temporal allocation data files.

9.2.1 Master Sector Code (MSC)

In order to facilitate reporting and merging of data using different sector classification codes, a five digit master sector code (MSC) system was developed. These codes were then assigned to all SCC codes in the BQF files as the data records were entered. The MSC system was designed so that emissions data could be reported on three different levels:

Category: the first digit specifies the emission category

1	Industrial
2	Stationary fuel combustion
3	Solid Waste incineration
4	Transportation
5	Open Sources

Sector: the next two digits specify the sector, for example, in fuel combustion sources,

01	Electric Power Generation
02	Industrial Fuel Combustion
03	Commercial Fuel Combustion
04	Residential Fuel Combustion
05	Residential Wood Combustion
06	Other Wood Combustion
07	Stationary Internal Combustion

Sub-sector: the final two digits specify further detail in a given sector; for example in electric power generation,

01	Bituminous Coal Combustion
02	Residual Oil Combustion
03	Distillate Oil Combustion

The full master sector code system is documented in Appendix F.

9.2.2 Base Quantities and Activity Levels (BQF)

The calculation of the annual emission database for the toxic inventory was done by integrating base quantity data, from BQF files with the EFF files. Separate point and area BQF files were implemented to account for point specific and regional anthropogenic toxic chemical emissions. All sectors covered in this inventory, except agricultural pesticide application emissions (Section 8), have activity level data assembled in the BQF files. Although some sectors appear as both point and area sources the BQF data merging procedure were checked manually to ensure that activity levels were not included more than once for a given sector/grid.

Three point source files were used for this study. The U.S. and Canadian (excluding Ontario) data were obtained from the U.S. EPA, and the Ontario data were obtained from the OME. The Canadian file contained data supplied to the US from Environment Canada (C & P) for the NAPAP criteria pollutant inventory. Both point source files from the U.S. EPA were reduced to the specific SCC codes associated with the sectors covered in this inventory. The Ontario file was not reduced to the required SCC's, but was used directly after linking with MSC codes. A list of SCC codes, grouped by MSC codes, is provided in Appendix F for both point and area sources.

In processing the 1985 NAPAP selected point source file, the following processing steps were performed to merge all required data into the BQF point source file:

- Stack temperature, height, diameter and flowrate were converted to SI units
- Modelling grid locations were calculated from latitude and longitude (lower left corner is I,J = 1,1)

- Ontario point sources were assigned UTM grid numbers (based on latitude and longitude), for points outside of Ontario, UTM grid numbers are equal to zero
- Records with zero throughput and those outside of the modelling domain were removed from the inventory
- Master Sector Codes (MSC) were assigned to the appropriate SCC codes
- Separate emission factor profiles by individual species or congener with CAS code identification were assigned for PAH's and the chlorinated compound classes (the latter profile includes PCB, PCDD, PCDF) to each point
- Data uncertainty codes were assigned to base quantity (emission factor quality indicator codes were assigned by individual species) values indicating the source of information or quality of information

Some point sources required special pre-processing before merging with the point source BQF file. Specifically the SCC codes for Iron and Steel (MSC 10201) were manually selected for individual plants in the U.S.

The file structure and database field descriptions are presented, for point and area BQF files, in Section 9.3.

The area source activity level and base quantity data were gridded to the inventory domain and keyed to MSC separately for Ontario, Canada (less Ontario), and the US. Because area source base quantities were not supplied in NAPAP files, it was necessary to back-calculate basic quantity data by SCC, using the information supplied. For the majority of area source US SCC codes, the following pre-processing was done:

- County level base quantities were back-calculated from SCC specific criteria pollutant emissions and supplied criteria pollutant emission factors. Although this calculation was done for all criteria pollutants, base quantities derived by NO_x and particulate emissions data were found to be most consistent and were used directly,
- Units of base quantities were converted to SI,

- US county centroid latitude and longitude data from the county centroid file (supplied by US EPA) were merged with county base quantities, and modelling grid locations calculated by centroid,
- Base quantities were then summed by state, SCC and grid cell,
- Data were assigned MSC by SCC and appropriate PAH and chlorinated compounds emission factor profiles by MSC, also, data quality codes were assigned to base quantity values indicating source of information or data quality.

Some sectors required further special processing before merging with the BQF file. These were:

- US residential wood combustion data were apportioned to fire place (MSC 20502) and wood stove (MSC 20501) using state specific fractional usage factors,
- Mobile highway travel sectors (MSC 40101, 40201, 40401) base quantities were derived from county fuel usage information supplied by US EPA, and available vehicle class fuel economy data,
- All landfill emission (Ontario, Canadian, and US) (MSC 50701) were calculated on a per capita basis. Base quantities for this sector were derived directly from population data,
- Transformers/Capacitors leakage/spillage (MSC 50601) for US and Canada were calculated on a per capita basis. Base quantities were derived, as for MSC 50701, from population data.

The U.S. area source gridded base quantities were then read into the area BQF file. For the Canadian area source sectors (omitting Ontario), which also were lacking base quantities as well as spatial resolution in the NAPAP files, the following pre-processing was done, based on Canadian SCC codes:

- Base quantities were back-calculated from criteria pollutant emissions and literature-derived emission factors for the criteria pollutants (i.e., mostly AP-42 and reported Canadian emission factors),

- Provincial activity levels were spatially allocated using gridded surrogates (apportioned to the modelling grid by centroid) provided by Environment Canada (C & P); the only exception being base quantities for forest fires were gridded using US EPA spatial surrogates for combined forests,
- Unit conversions to some sector base quantities were required,
- Data were assigned MSC by SCC and appropriate PAH and chlorinated compounds emission profiles by MSC; data quality codes were also assigned to base quantities values.

Canadian mobile area source base quantities for light duty gas vehicles (MSC 40101, SCC 21100) were further divided into three new categories; SCC 21500 - leaded fuel, SCC 21510 - 3-way Catalyst, SCC 21520 - oxidation catalyst. Emission profiles were assigned by SCC code instead of MSC. The Canadian data were then merged with the US data in the BQF area source file.

Ontario area source base quantity data apportion on the UTM grid system were obtained from the OME for this inventory. Ontario SC codes were selected and assigned Canadian SCC codes, MSC codes and emission profiles. The gridded base quantities were converted to appropriate units for merging with the area source BQF file. Special pre-processing was required for some Ontario area source categories:

- The mobile sectors for Ontario (SC 1-13, 90, 91) were merged to form MSC 40101, 40201, and 40401 (SCC 21200, 21400, 21500, 21520, 21200, 21400),
- Residential wood combustion (SC 54) was allocated to wood stoves and fire places (MSC 20501 and 20502),
- Finally, asphalt hot mix (MSC 50301) was extracted from the Canadian criteria pollutant file (US EPA), converted to a base quantity value and apportioned by population into the Ontario UTM grid system.

Ontario base quantity data (with modelling grid coordinates set to zero) were then merged with US and Canadian area source data in the BQF area file.

9.2.3 Emission Factors

Emission factor profiles for PAH were prepared separately from PCB, PCDD, and PCDF (pesticides were entered directly as emission values, see Section 8). As the profiles were entered, file numbers were assigned (100's for PAH profiles, 200's for PCB, PCDD and PCDF profiles). The file numbers were then matched in the BQF files with specific sectors MSC or SCC codes for both point and area data. Entry of the profile data was manually checked after entry.

A complete report on file numbers, descriptions, and units is provided in Appendix F. The individual toxic chemical emission factor profiles, by file number, are provided in Appendix A.

9.2.4 Temporal Allocation Factors (TFF)

The total emissions reported in the annual emissions inventory were temporally resolved for modelling purposes. The temporal factor file (TFF) was designed to allow allocation of annual toxic chemical emission data to produce hourly emission values for typical weekday, Saturday, or Sunday scenarios of each season. For purposes of the toxic inventory the season definitions are similar to the NAPAP 1985 emissions inventory (US EPA 1989b):

Season	Months
Winter	December, January, February
Spring	March, April, May
Summer	June, July, August
Fall	September, October, November

Seasonal factors divide the annual total emissions into emission values for the four seasons. The four seasonal emissions are further resolved using three daily factors to represent the typical weekly operations schedules. Twenty-four (24) hourly factors, based on daily operation schedules, reduce the emissions to hourly values. Thus, the hourly emission of a specific pollutant can be calculated by:

hourly emission = annual emission x seasonal factor
x daily factor
x hourly factor

The seasonal and hourly factors sum to unity. Since the seasons are based on a duration of 13 weeks the daily allocation factors sum to unity as:

(65 x weekday factor) + (13 x Saturday factor) + (13 x Sunday factor) = 1

The temporal allocation factors are in local standard time (LST) (e.g. hour 1 corresponds to the period midnight to 1 a.m. local time). For modelling applications the temporally resolved emissions are converted to Greenwich Mean Time (GMT) using gridded time zone offset data which are provided in the database. This produces a standardized set of emissions for both point and area sources.

The U.S. point source files received from the U.S. EPA contained operating information specifying the seasonal variation (as a percent), days per week of operation and number of hours per day of operation. In processing the 1985 NAPAP data the following checks were made: seasonal factors were used directly as fractions, where available, processes that did not report correct seasonal breakdowns (i.e.,. they did not sum to one) were assigned a uniform seasonal profile (equally distributed to all seasons), finally, point sources with missing weekly process operation data were assigned a uniform profile. All other daily factors for typical weekly operations were calculated based on days of operation as follows:

Days/wk	Emissions Allocated to:
1	Saturdays only
2	Saturdays and Sundays, equally
3-5	Equally on weekdays only
6	Equally on weekdays and Saturday
7	Equally on all day of the week

The hourly factors were calculated based on the number of hours per day of process operation. For point sources without process operation schedules a uniform profile was assigned. All other hourly temporal factors were calculated using the following method:

Hours/day	Emission Allocated to:
1-17	Zero for midnight to hour 7 (LST) and then equally for all hours of operation beginning with hour 8 (LST)
>17	Equally among 24 hours of day

The Canadian (excluding Ontario) point source emission factor profiles supplied to the US EPA for the NAPAP inventory by C&P of Environment Canada were applied directly to the selected point sources used in this emission inventory.

Ontario point source temporal factors were not supplied with the point source data. The temporal allocations file has been left empty (i.e., as zero) for these points. The model file processing checks for proper temporal variation for all points and assigns a default flat profile for missing temporal data.

Area source temporal codes were compiled at the state, grouped state or national level depending on the relative contribution of the sector and availability of data, for the NAPAP 1985 emissions inventory. The same

values were applied to other Canadian provinces in the toxic chemical inventory.

Some open sources developed for this inventory, such as pesticide application, landfills, and transformer storage, had sector specific and/or geographically specific temporal codes developed (see relevant sections of this report). The temporal codes for these sectors were entered directly into the TFF files.

Processors have been developed for generating hourly modelling emissions files on the 127 km grid for a specific species. If more than one species is to be modelled simultaneously, then the processor must be run for each species, so providing a gridded file for each species for each hour.

9.3 PC/Focus Data File Structures

The annual toxic chemical emissions inventory is comprised of three types of PC/Focus files; the BQF (base quantity) files (BQAREA, BQPOINT3), the emission factor file (EFFACT), and the emission files (EMAREA, EMPOINT4). Point or area source data are entered into the base quantity files along with source classification fields (SCC, MSC) and appropriate emission factor file numbers. New emission factor profile files can be created and cross referenced in the BQF files as new point and area sources are entered. The PC/Focus file structures for the BQF and EFF files are presented in Figures 9.3.1 to 9.3.3.

By multiplying the base quantities (BQF) and the appropriate emission factors (EFF), the annual emissions files are produced for point and area sources. The PC/Focus file structures for the area and point annual emission files are presented in Figure 9.3.4 and Figure 9.3.5. The field used in the area and point source files (both BQF and annual emission) are described in Table 9.3.1. The fields appearing in each file are indicated for BQF (point & area), and Emission (point & area). The EFF file fields are described in Table 9.3.2. All files have a date field indicating the entry date or last update. Other segments with fields not described in these tables are cross reference look up files for CAS names, EFF file descriptions, MSC descriptions and units, quality flag descriptions, NEDS state code names, and SCC code descriptions.

TABLE 9.3.1

Point and Area Source, BQF and Emissions File Field Descriptions

Fieldname	Description	BQF		Emission	
		Area	Point	Area	Point
STATE_CODE	NEDS State Code	X	X	X	X
CMC_IJ	Modelling grid I,J (as IIJJ)	X		X	X
UTM_GRID	UTM grid number	X	X	X	X
SCC_CODE	SCC code (CDN & US)	X	X	X	X
MSC_CODE	MSC Master Sector Code	X	X	X	X
PAHEFF	PAH profile file number	X	X	X	X
PCBEFF	PCB (and others) profile number	X	X	X	X
TEMPORAL	Temporal reference code	X		X	
BASE_QUANT	Base Quantity or Activity Level	X	X		
QFBQ	Data Quality Flag (base quantity)	X		X	X
UPD_DATE	Last update date (or LAST_UPD)	X	X	X	X
COUNTY	NEDS county code		X		X
PLANT_CODE	Plant ID code		X		X
POINT_CODE	Point ID code		X		X
CMC_I	Modelling grid coordinate I		X		
CMC_J	Modelling grid coordinate J		X		
LATITUDE	Decimal latitude location		X		X
LONGITUDE	Decimal longitude location		X		X
STACK_HT	Stack height (m)		X		X
STACK_DIA	Stack diameter (m)		X		X
STACK_T	Stack temperature (C)		X		X
STACK_FLOW	Stack Flow (m^3/s)		X		X
SIC_CODE	SIC Code (Ontario only)		X		X
PROCESS_NAME	Process name (Ontario only)		X		X
PRODUCT	Product (Ontario only)		X		X
PLANT_NAME	Plant name (Ontario only)		X		X
CITY_NAME	City (Ontario only)		X		X
CHEM_ABS	CAS (Chem. abstract number)			X	X
EMISSION	Emission value (mg)			X	X
QFEF	Emission factor quality flag			X	X

TABLE 9.3.2
Emission Factor File Field Descriptions

Fieldname	Description
EMISS_NUM	Emission profile file number (linked with PAHEFF & PCBEFF)
DATE	Last update date (for all species in profile)
CHEM_ABS	CAS (chemical abstract index number)
EMISSFAC	Emission factor (mg/BQ units)
RCAS1	Cross reference 1 to other CAS numbers included in factor
RCAS2	Cross reference 2 to other CAS numbers included in factor
RCAS3	Cross reference 3 to other CAS numbers included in factor
QUALITY_FL	Emission factor quality code (becomes QFEF)

FIGURE 9.3.1

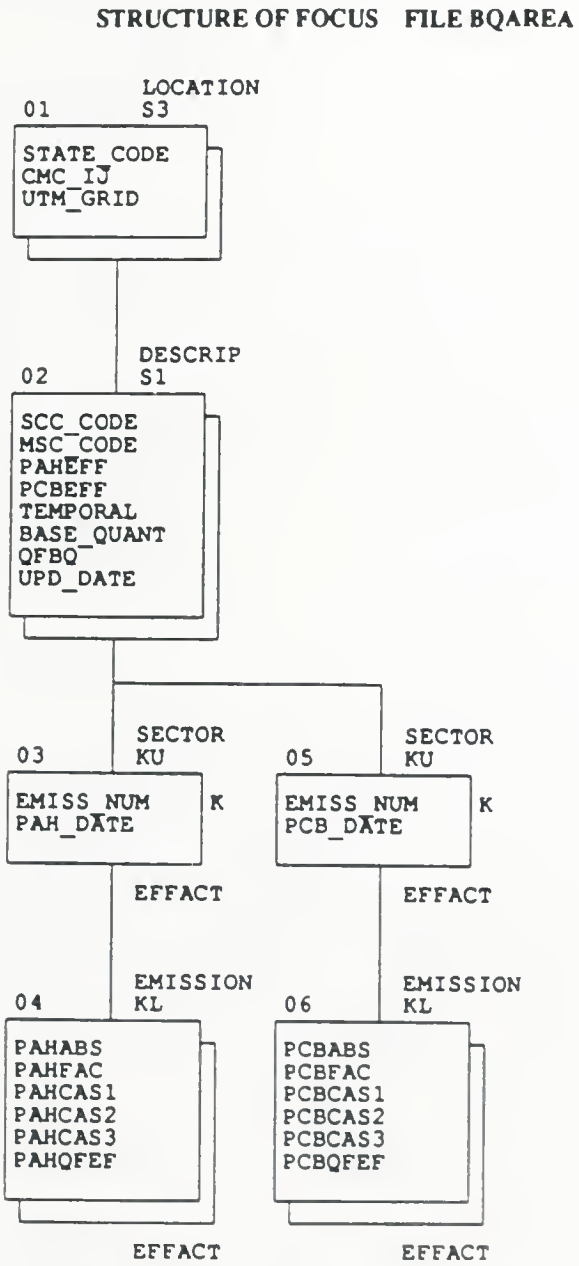

STRUCTURE OF FOCUS FILE BQAREA
LOCATION
01 S3
STATE_CODE
CMC_IJ
UTM_GRID
DESCRIP
02 S1
SCC_CODE
MSC_CODE
PAHEFF
PCBEFF
TEMPORAL
BASE_QUANT
QFBQ
UPD_DATE
SECTOR
03 KU
EMISS_NUM K
PAH_DATE
SECTOR
05 KU
EMISS_NUM K
PCB_DATE
EFFACT
EFFACT
EMISSION
04 KL
PAHABS
PAHFAC
PAHCAS1
PAHCAS2
PAHCAS3
PAHQFEF
EMISSION
06 KL
PCBABS
PCBFAC
PCBCAS1
PCBCAS2
PCBCAS3
PCBQFEF
EFFACT
EFFACT

FIGURE 9.3.2

Structure of Focus File BQPoint3

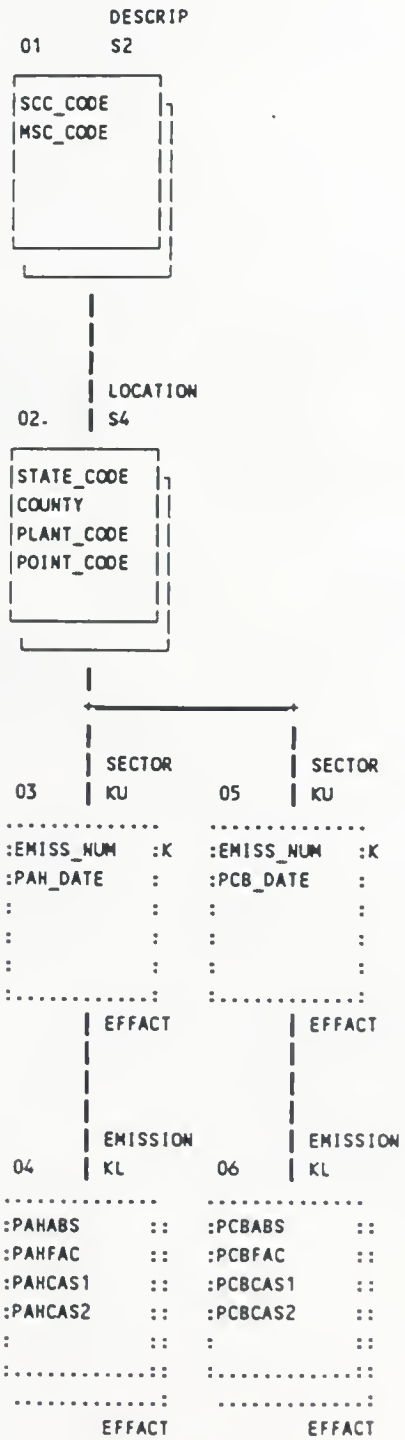


FIGURE 9.3.3

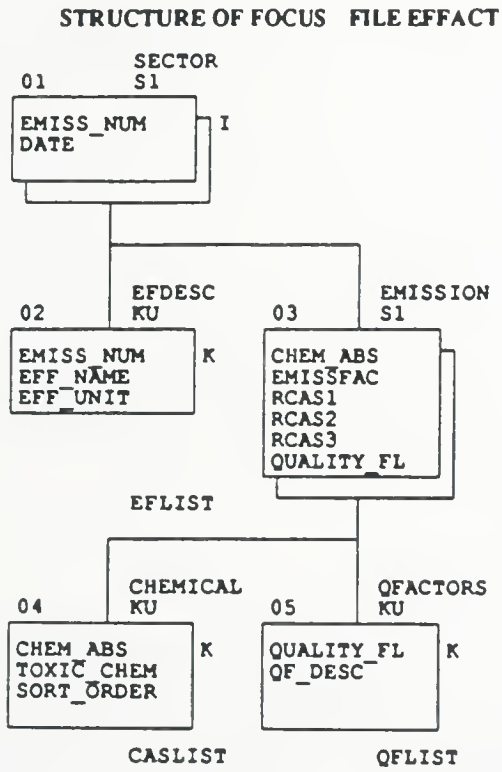

STRUCTURE OF FOCUS FILE EFFACT
SECTOR
01
S1
EMISS_NUM
DATE
I
EFDESC
02
KU
EMISS_NUM
EFF_NAME
EFF_UNIT
K
EMISSION
03
S1
CHEM_ABS
EMISSFAC
RCAS1
RCAS2
RCAS3
QUALITY_FL
EFLIST
CHEMICAL
04
KU
CHEM_ABS
TOXIC_CHEM
SORT_ORDER
K
QFACTORS
05
KU
QUALITY_FL
QF_DESC
K
CASLIST
QFLIST

FIGURE 9.3.4

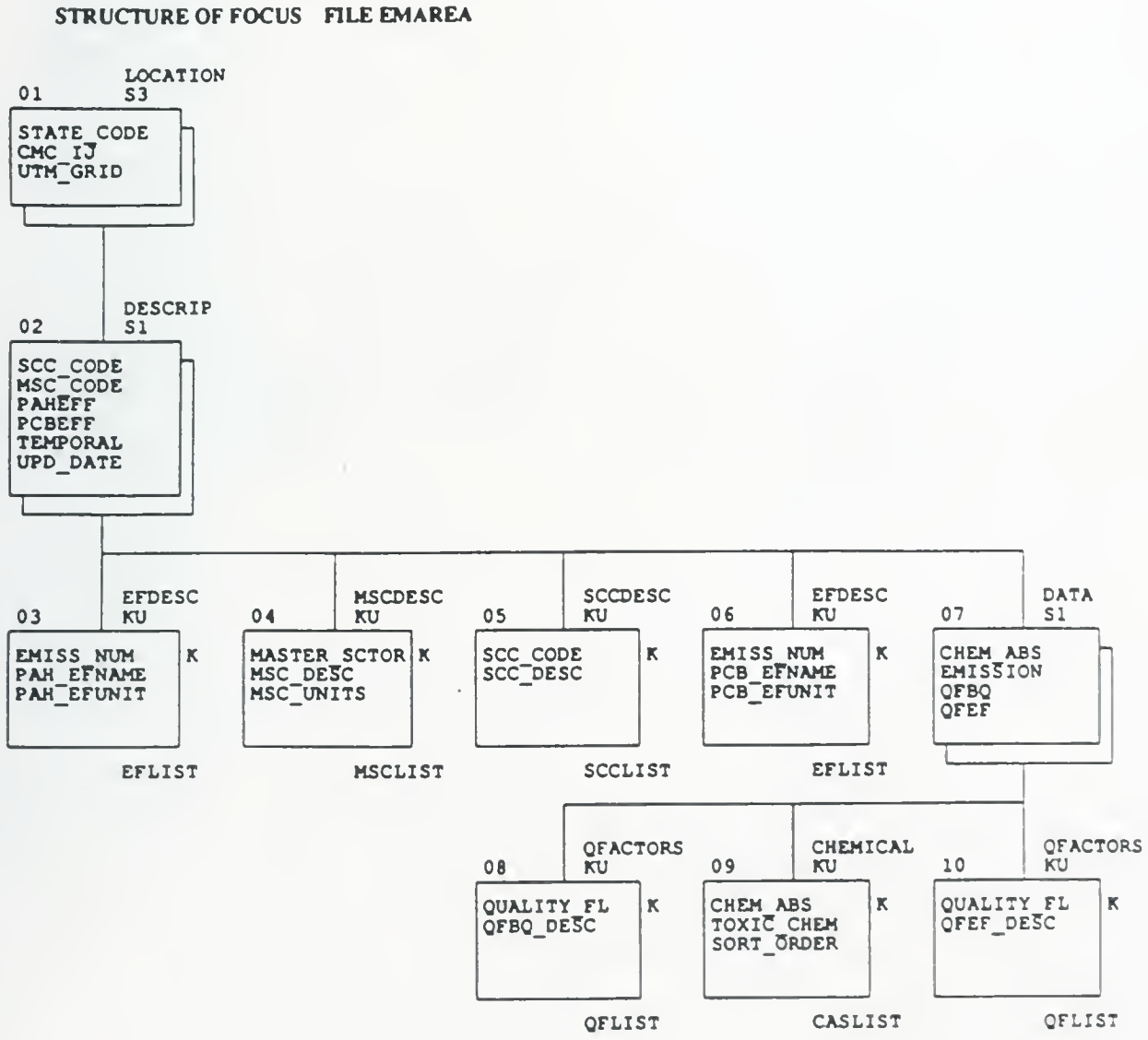
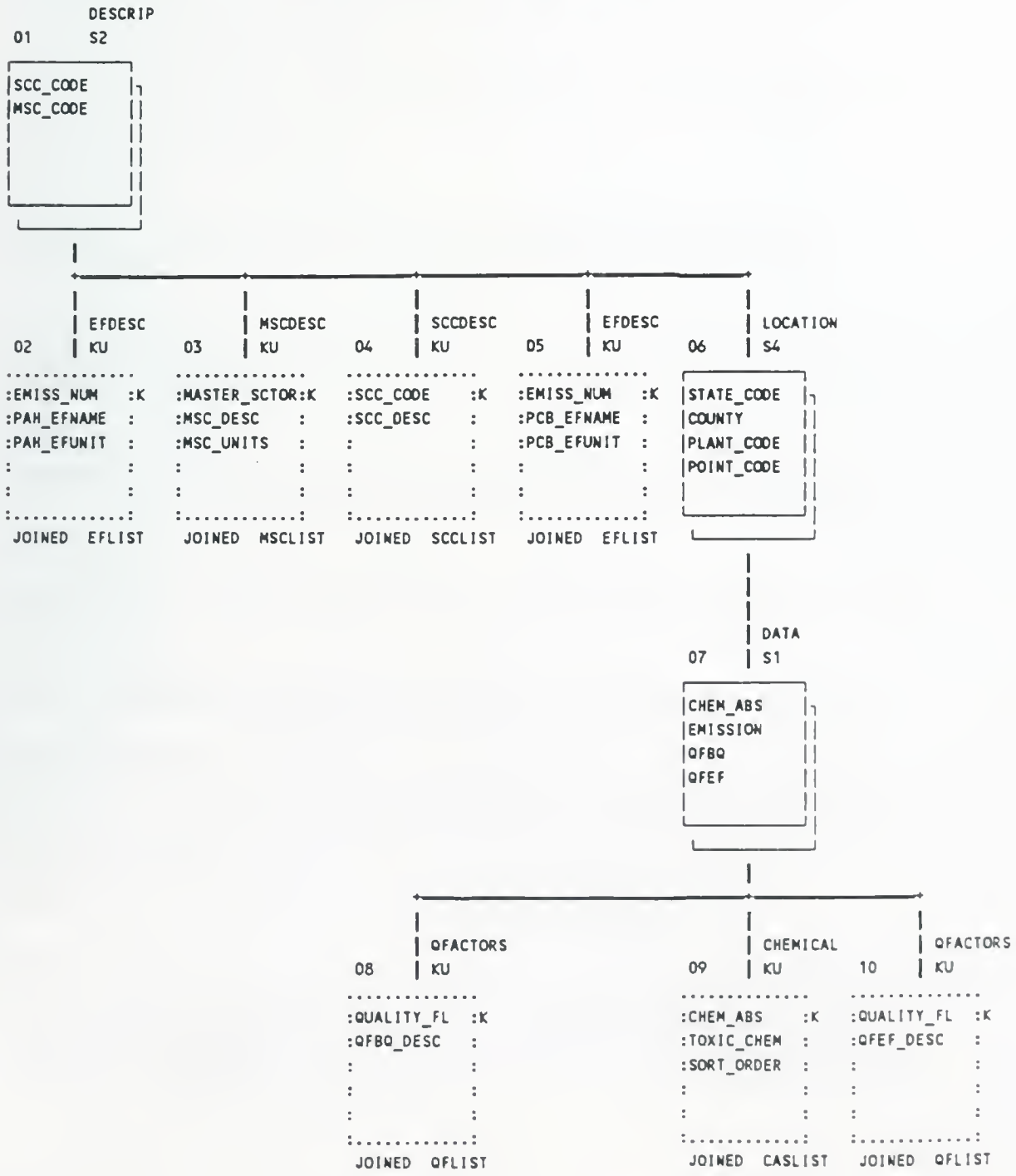

STRUCTURE OF FOCUS FILE EMAREA
LOCATION
01 S3
STATE_CODE
CMC_IJ
UTM_GRID
DESCRIP
02 S1
SCC_CODE
MSC_CODE
PAHEFF
PCBEFF
TEMPORAL
UPD_DATE
EFDESC
03 KU
EMISS_NUM K
PAH_EFNAME
PAH_EFUNIT
EFLIST
MSCDESC
04 KU
MASTER_SCTOR K
MSC_DESC
MSC_UNITS
MSCLIST
SCCDESC
05 KU
SCC_CODE K
SCC_DESC
SCCLIST
EFDESC
06 KU
EMISS_NUM K
PCB_EFNAME
PCB_EFUNIT
EFLIST
DATA
07 S1
CHEM_ABS
EMISSION
QFBQ
QFEF
QFACTORS
08 KU
QUALITY_FL K
QFBQ_DESC
QFLIST
CHEMICAL
09 KU
CHEM_ABS K
TOXIC_CHEM
SORT_ORDER
CASLIST
QFACTORS
10 KU
QUALITY_FL K
QFEF_DESC
QFLIST

FIGURE 9.3.5

Structure of Focus File EMPoint4



9.4 PC/Focus Database Generation and Reporting

Source code listings of example PC/Focus procedures used to generate the annual emissions inventory and the subsequent reporting routines are provided in Appendix F, along with the master file descriptions. The reporting procedures demonstrate the use of MSC to report totals and sub-totals. The following is a brief description of the example procedures included with the inventory:

EMAREA.FEX
updates the area source emission file (EMAREA) since last update (&sincedate) using area source BQF file (BQAREA) and the EFF file,

EMAREA2.FEX
reads in prepared pesticide emissions data to the EMAREA file (both US & CDN, and Ontario),

EMPOINT.FEX
update the point source emission file (EMPOINT) since the last update (&sincedate) using the point source BQF file (BQAREA) and the EFF file,

TOXREP.FEX
generates a subset of the annual emissions files (TOXREP) for further report generation,

TOXREPAR.FEX
batch processor for area source emission reports (EMREP1 to EMREP6),

TOXREPPT.FEX
batch processor for point source emission reports (EMREP1 to EMREP6),

TOXREPCB.FEX
batch processor for point & area source emission reports (EMREP1 to EMREP6),

EMREP1.FEX
generic totaling of emissions by chemical abstract number (CAS) and subtotalled by major classes (Note: units, record selections, titles, and reporting file [EMAREA, EMPOINT, or TOXREP] are variable parameters for EMREP1 to EMREP6, see batch processors for example parameter values),

EMREP2.FEX
generates table of SCC codes by MSC,

EMREP3.FEX
generic totaling of chemical class emissions (across the page) by MSC codes,

EMREP4.FEX
generic chemical class emission totaling by MSC code and sub-totaled by major sector,

EMREP5.FEX
generic totaling of class emissions (across the page) by SCC codes,

EMREP6.FEX
generic totaling of class emission (across the page) by major sector,

EFFREP1.FEX
generates emission factor file report on individual emission factors for each file number,

EFFREP2.FEX
generates a table of emission factor file descriptions and units by file number,

EFFREP3.FEX
sums the class emission factors (PAH, PCB, PCDD, PCDF) by emission file number,

EFFREP.FEX
batch processes all three EFF reports

TMPPT.FEX
point source modelling file processor processes one season/day for one toxic chemical species)

TMPPEST.FEX
pesticide modelling file processor (produces one season/day for one pesticide)

TMPAR.FEX
area source modelling file processor (produces one season/day for one toxic chemical species)

10. INVENTORY RESULTS AND EMISSION SUMMARY REPORTS

Total annual estimated emissions by compound class and individual species have been computed at the SCC level for point and area sources in Ontario, other Eastern Canadian Provinces and the Eastern United States, using available data. These emissions have also been temporally and spatially apportioned to the grid structures for Ontario and Eastern North America. In view of the large amount of inventory data, all results at the SCC level are provided in appendices to the report and aggregated data by sector or general emission category are discussed in the text. Codes used for aggregation are provided in the appendix to the report (e.g., corresponding SCC's assigned to sector codes, etc.)

Graphical summaries of the gridded results of the inventory compilation where appropriate are provided on three scales of detail. The first scale covers southern and central Ontario UTM grid only; the second scale of detail covers the whole of the Ontario UTM grid; and finally, the entire Northeastern grid is provided with Ontario plotted on the UTM grid and the remaining provinces and the U.S. on the 127 km polar stereographic grid. In view of the variable grid sizes in each of these presentations (i.e., variable UTM grid in Ontario and 127 km outside), the emissions must be presented as fluxes (mass.km^{-2}.yr^{-1}) in order to meaningfully represent the spatial distribution in these graphical summaries.

All fluxes are based on the 'true' grid area rather than the rectilinear 127 x 127 km polar stereographic area (= 16 129 km^2). The correction factor or area map-factor varies from 1.0 at latitude = 60°N to 0.52 at 20°N.

A summary of the total emissions by compound class and general emission category are shown in Table 10.1.1 for Ontario and Eastern North America (including Ontario). It can be seen that the estimated PAH emissions were several orders of magnitude greater than the other classes of compounds

and that Ontario sources contributed approximately 2.9% of the total Eastern North America emissions for all pollutants combined. By examining the data, the relative Ontario contribution is shown to vary significantly for the different compound classes and source categories (e.g., range of 2.9 to 11.3% contribution for compound class totals) which, in part, reflects the predominance of specific types of sources in some areas, the year-specific conditions and the lack of certain types of sources in Ontario and other areas as well as the variability of data. The relative Ontario contribution of PCDD and PCDF is highly uncertain for specific industrial and open source categories. It should be noted that the total population of Ontario represents approximately 4.5% of the population within the entire Eastern North American grid. Thus, on the basis of population, somewhat greater relative emissions of PAH in Ontario might have been expected than found in this initial compilation.

10.1 Ontario Emissions

Sector contributions of these compound classes in Ontario are shown in Table 10.1.2 and Ontario point and area source sector contributions by each class are shown in Tables 10.1.3 to 10.1.6 which also indicate a ranking of sector strengths. For most sectors, the assigned uncertainty to the estimated emissions (see Section 3.10) ranged from C to E with only a limited number of more accurate ratings (i.e., B) for individual sources within sectors. This indicates rather substantial uncertainties in the specific emission values shown, but these data usually provide a clear indication of the relative importance of sectors. The assigned uncertainty ratings to emission factors and base quantities by SCC are provided in the appendix.

From results in Table 10.1.2, it is clear that residential wood combustion emissions (i.e., especially from wood stoves) were found to predominate other sources of PAH emissions and estimated to account for approximately 50% of the annual Ontario PAH emission total. Both the emission factors and the consumption of wood stoves are reportedly greater in stoves than fireplaces or furnaces. Ferroalloy production and metallurgical coke production were estimated to contribute 20 and 10%, respectively, of annual emissions of PAH in Ontario. However, significant uncertainties exist for the ferroalloy source contribution which would require an in-depth evaluation of the types of furnaces in use, coke consumption, types of alloys produced, etc. Other significant PAH sources, of approximately the same emission magnitude to each other, included on-road diesel vehicles, gasoline-powered vehicles, coal-fired electric power stations and prescribed burning. It has been noted in earlier sections that the acreage burned by forest fires in Ontario during 1985 was the lowest recorded (for the past 30 years) and a much more significant contribution by wildfires to these types of pollutants would occur in other years (e.g., at least two orders of magnitude greater on average). The predominant source of PCB emissions was estimated to be leakage from transformers and other electrical equipment, followed by lesser

emissions from coal combustion in electric power generating stations, industrial fuel combustion, and volatilization from landfills. It should be recognized that emission factors were not available for transformers or landfills; contributions in the inventory are based on estimation methods detailed in the text and actual emissions attributed to these sources could differ substantially. However, the actual locations of PCB storage areas are well defined in Ontario. Municipal incineration, secondary copper production and residential wood combustion were found to be the major sources of PCDD and PCDF. These data include emissions from the Commissioner Street refuse incinerator which has since been closed. Significant PCDD and PCDF emissions have been measured from limited testing in secondary metal cupola furnaces, depending on the types of feed materials (e.g., PVC content, etc.). Without a thorough characterization of specific point sources for such emissions, the contribution of these pollutants by this sector is highly uncertain. Of particular importance, the contribution of residential wood combustion to the PCDD and PCDF pollutant classes has been based on very limited chimney particulate analyses and reported total particulate emission factors. Most testing of wood stoves has focussed on particulate and PAH measurements. In addition, other potential sources of PCDD emissions in Ontario, which could not be quantified (see Section 11.2), may be as significant as the total PCDD amounts shown. Hence, it is evident that a large portion of the emission totals for each compound class result from relatively few types of sources and, in some instances, large relative contributions from collective area sources. For example, emissions attributable to residential wood combustion were significant for each of the compound classes which are of particular seasonal importance.

Results in Table 10.1.7 indicate the total estimated emissions of individual toxic chemical species in Ontario. The magnitudes of these, in part, reflect those species most often measured in emission testing. Thus, some relatively low values may be partly due to lack of measurement as well as the actual profiles found in the source measurements. It can be seen that

the largest PAH constituent emissions are often the most volatile species of the PAH compounds selected (e.g., acenaphthylene, methylphenanthrenes, phenanthrene, fluoranthene, pyrene) and are the components most often found in emissions. The actual relative amounts of these also depend on whether or not source measurements used to derive emission factors have included both the vapour and particle fraction and have efficiently retained vapours during sample collection. One of the more toxic PAH species, namely benzo(a)pyrene, was found from this emission compilation to account for 1.9% of the total sum of the selected PAH species. A smaller relative B(a)P fraction would, no doubt, have been determined if naphthalene was included in the inventory, since naphthalene is reported to be predominant in some combustion-related emissions. However, it is not classed as a toxic chemical and has been excluded. On the other hand, there was little information (i.e., emission measurements) available for some of the nitro-PAH species included in the inventory (e.g., 1-nitropyrene, carbazole, dibenz(ah)acridine) and such components were reported or found only in emissions from coal-fired power generating stations, coke ovens and gasoline vehicles. For the chlorinated compound emissions, very limited data were available regarding the species of PCB emission sources as most investigators have reported total PCB only. Where available, speciated PCB information for specific sources is contained in the database. It is evident from this compilation of dioxin species that greater amounts of the penta, hexa and hepta PCDD congeners were emitted than the fully chlorinated OCDD. Similarly, most of the total furan emissions comprised the tetra, penta and hexa PCDF congeners. The amounts of PCDD and PCDF listed under congeners in Table 10.1.7 were unspeciated totals reported for some sources. A total of 57 grams of 2,3,7,8-T_4CDD was estimated to be emitted in Ontario during 1985, based on available data; this total is a minimum estimate in that speciated emissions are not always available.

The estimated annual emissions have been gridded on the variable-sized UTM grid for Ontario, as shown in Figures 10.1.1 to 10.1.8, representing emission flux densities of area sources and combined point and area sources. It can be seen that the greatest emission densities of the combustion-related emissions (i.e., PAH, PCDD and PCDF) are located in areas of highest population, due to sources such as residential wood and other fuel combustion, and on-road vehicles. For example, greater emission densities have been determined, and can be visually detected in these maps, in the major urbanized areas and major transportation routes such as Highway 401 and QEW that coincide with the smallest (5 x 5 km) UTM grids.

Figures 10.1.9 to 10.1.12 show the distributions of pesticide emissions on the UTM grid estimated for southern and central Ontario according to pesticide use; i.e., herbicides, insecticides, fungicides and nematocides.

The following breakdown by crop-type of pesticide use in Ontario for all pesticides surveyed by McGee (1983) has been extracted from the survey results:

	Insecticides kg	Herbicides kg	Fungicides kg	Nematocides kg
Field crops	186,610 (43.3%)	5,411,260 (97%)		1,610,610 (100%)
Fruit	143,760 (33.4%)	7,890 (0.1%)	410,990 (72.7%)	
Vegetables	100,500 (23.3%)	100,900 (1.8%)	154,720 (27.3%)	
Roadsides		58,130 (1.0%)		
	430,870	5,578,180	565,710	1,610,610

The first three of these pesticide groups are extensively used throughout southern Ontario, as well as the central regions, while the use of nematocides is concentrated mainly in Southwestern Ontario where tobacco is grown. Insecticides are heavily used on apples, grapes and peaches in the fruit growing areas, particularly Niagara County. Insecticides are also extensively used on vegetables and field crops, and this is reflected in the distribution of their emissions in Ontario. Fungicides are mainly used on fruit crops, predominantly in Niagara County.

The pesticide emissions for Ontario in Table 10.1.2 overwhelm those in the other four combustion-related pollutant classes with a total estimated emission of ~2,700 tonnes for those pesticides studied, compared to a total of 196 tonnes for the other chemical classes.

The pesticides in Table 10.1.7 have been grouped into herbicides, insecticides, fungicides and nematocides. From this table, it is seen that approximately 57% of these emissions are due to soil fumigants; herbicides contribute 39% of the emissions with the insecticides and fungicides, which have been included in the inventory, contributing approximately 12% and 3%, respectively.

The highest ranking pesticide is the combined dichloropropane/ dichloropropene soil fumigants, almost all of which was applied to tobacco. In the soil, these fumigants have a relatively short half-life (16 days). However, due to their high vapour pressure they rapidly volatilize and their decomposition in air through photolysis and chemical reaction with other pollutants will be important.

Of the herbicides, the high ranking of atrazine (1), alachlor (2) and metolachlor (4), are due to their use on field crops and soybeans, while 2,4,-D ranks third and is mainly used on grains.

Of the insecticides studied, the highest emissions are due to carbaryl which is used mainly on fruit crops. The emissions of the persistent pesticides chlordane and lindane are due to agricultural application and do not include termite control uses (chlordane) or seed pre-treatment (lindane); only lindane used on tobacco crops and chlordane used on corn are included in the inventory. However, in the case of chlordane, the emissions from soil treatment, where the insecticide is injected into otherwise undisturbed soil, will be very small since chlordane is relatively immobile in soils. Lindane, on the other hand, is very strongly bound to soil organic matter and, where applied as treated seed, emissions due to the current planting will be small. However, due to the persistence of lindane, tilling of the soil for subsequent plantings will expose previously applied lindane, resulting in emission due to volatilization. Extensive data on lindane residues in soils would be required to estimate this component of lindane emissions.

The fungicide captan is used mainly on fruit and has low persistence in soils. The fungicides metiram and mancozeb are also used for fruit and vegetable crops. However, these mixtures containing organo-zinc compounds have negligible vapour pressures and do not volatilize in significant amounts. They are also of low persistence and it is likely that their degradation products would be the main contaminants entering the atmosphere.

10.2 Emissions on the Eastern North America Grid

The estimated annual emissions by pollutant class and sector in Eastern North America (ENA including Ontario) are presented in Table 10.2.1. A comparison of the strongest ranking sectors in Ontario and ENA are also shown in Table 10.2.2. The contribution by residential wood combustion to total PAH emissions was found to be approximately 31% in ENA, followed by other major sources such as: primary aluminum production, industrial fuel combustion, open fires and vehicles. The ferroalloy sector emissions that result from coke consumption are very uncertain, since difficulties were encountered in associating base quantities for the different alloys with coke usage. It is interesting to note that the industrial waste incineration sector was estimated to represent the highest ranking type of PCDD emission source. However, because emission factor data are limited for industrial incinerators and the types of wastes burned are highly variable, there is considerable uncertainty associated with the emission totals shown and rank of this sector. Similar comments apply to the PCDD contribution by residential wood burning, since most emission testing efforts for these toxic chemicals have focussed on municipal waste incinerators in which emissions are better defined. PCDD and PCDF emissions from secondary copper production could be considerably underestimated for areas other than Ontario, due to insufficient point sources identification and base quantity information. Alternatively, the Ontario emissions from such sources could be overestimated.

For comparison purposes, emissions by category and point/area source contributions are also shown for Ontario, other Canadian provinces and the portion of the United States within the modelling grid (see Table 10.2.3). It is evident that in the U.S., point and area sources amount to approximately equal contribution for most of the pollutant classes; while in Ontario, area source contributions are predominant for PAH and PCB emissions. This partly reflects differences in the types of source contributions, but also

differences in inventory methodologies. For example, many more types of emission sources are classified as point sources in the U.S. inventories (e.g., NAPAP) than in the Ontario and Canadian inventories. That is, most Canadian stationary fuel combustion sources are collectively included as area sources (without regard to individual boiler sizes). In each geographical area, solid waste incinerator point sources were found to represent the strongest PCDD and PCDF emission sources. One major sector of PAH emissions, primary aluminum smelting/production, does not exist in Ontario; whereas, several aluminum smelters within the grid occur in Quebec and the U.S. It should be noted that the estimated PAH emissions for aluminum smelting in Quebec which are included in this study amount to approximately 50% of those estimated and reported in a recent Quebec PAH inventory that has been based on production capacities (Environment Canada, Quebec Region, 1988b). This anomaly, found after data processing, might have resulted from differences in production rates between the base study years, differences in deriving or applying process emission factors, or possibly incomplete selection of applicable SCC codes with corresponding base quantities from the NAPAP database in the current study. Although the reasons for this significant anomaly have yet to be found, it is quite evident that aluminum smelting represents a relatively strong source of PAH. The 'total' PAH emissions estimated for Quebec were reported to be 2,340 tonnes (Environment Canada, Quebec Region, 1988b). This amounts to ~28% of earlier estimates that have been made for the entire United States (Ramdahl 1981) and, thus, the Quebec estimates appear substantially higher than estimates in other studies.

The U.S. emission estimates of PAH in this study (i.e., gridded portion) have also been compared with previous inventory PAH compilations for the entire United States (see Table 10.2.4). The U.S. estimates have been reported in a recent Environment Canada study (Dann 1989) and other reports (NRCC 1983, Ramdahl et al 1981). This comparison is somewhat inappropriate since: the PAH species included in the earlier studies are not known (e.g.,

naphthalene, etc.), and some source emissions were not included in earlier U.S. estimates. In addition, the emission-related geographical coverage of the U.S. in the current study is estimated to represent approximately 70% of the entire U.S. (i.e., based on the fraction of criteria pollutant emissions in the grid area to the total U.S. emissions). Nevertheless, these comparisons provide a useful basis to indicate some relative source strengths and the magnitude of total estimated PAH emissions. Although the total emissions differ and the relative contributions for some of the major sources vary, emissions from residential wood burning represented the primary source in each of the studies (i.e., with a generally similar emission magnitude for this sector). Substantial differences in source strengths are evident for some of the other sectors (e.g., open burning, transportation), presumably due to differences in both base quantities and emission factors used in the estimates. In addition, very limited or no emission inventory data are available with which to compare the present emission estimates of PCB, PCDD, PCDF and pesticides.

The estimated totals of individual compounds and congeners of the toxic chemicals inventoried for ENA is presented in Table 10.2.5. Somewhat surprisingly, the largest amounts of PAH were found for pyrene, fluoranthene and anthracene, with lesser amounts of phenanthrene and methylphenanthrenes. The relative proportions of these species differ between Ontario and ENA, due to the more varied nature of PAH sources in ENA and differences in relative source contributions. In Table 10.2.6, a comparison has been made of the PAH species profiles determined from total emission estimates in this study with tabulated species in the 1985 NAPAP inventory and reported ambient air concentrations for measurements in Toronto during 1984 to 1986. It should be noted that the tabulated NAPAP data (U.S. EPA 1989b) were assumed to be emissions expressed in tonnes (i.e., no units provided with the tabulation). Similarly, it was assumed that the emission profiles were based upon species profiles obtained from the U.S. EPA emission speciation manual (U.S. EPA 1988).

The two PAH profiles provided in the manual are for tests conducted on catalytic and uncontrolled residential wood burning stoves and on a U.S. primary aluminum smelter. Hence, these NAPAP emission estimates may only represent a fraction of U.S. emissions of PAH. The ambient air mean concentration data were based on 42 vapour and particle phase samples collected during four seasons at an urbanized site in Toronto (Dann 1989). Such air measurements were also conducted at an urban site in Montreal. It can be seen that the ambient concentrations were highest for the most volatile PAH species (e.g., phenanthrene, fluorene, acenaphthylene, fluoranthene, pyrene) and the mean benzo(a)pyrene concentration accounted for ~0.6% of the species total. It is evident that the relative proportion of emissions data estimated in this study for Ontario match most closely with the Toronto PAH air concentration data for common constituents. A stronger correlation was found for the Ontario emissions of some constituents and the mean air concentrations measured during the winter in Toronto which may primarily reflect the impact of residential wood combustion on these air concentrations. Although less apparent at the Toronto site, a strong seasonal pattern (i.e., significantly higher fall/winter air concentrations than spring/summer) was found in the results for Montreal (Dann 1989). However, it should be recognized that some of these emissions data were based on particle phase measurements only. For example, on the basis of the reported ambient measurement results, it is probable that the emission compilations have not fully accounted for the more volatile PAH species (e.g., phenanthrene). Nevertheless, such comparisons provide at least a certain degree of confidence in these emissions data.

The estimated annual emissions for Eastern North America and Ontario have been gridded on the MOE modelling grid (see Figures 10.2.1 to 10.2.4). As might be expected, the patterns of the combustion-related emissions (PAH, PCDD and PCDF) are similar to the gridded pattern of NO_X emissions in the NAPAP study (U.S. EPA 1989b).

Table 10.2.7 also shows the total Eastern North American pesticide emissions. Only those pesticides for which both Canadian and U.S. data are available are included in the total. Table 10.2.5 indicates those pesticides for which U.S. data were not available. In total, approximately 33.1 kilotonnes of pesticide emissions have been inventoried for the Eastern North America grid for nine pesticides. An additional 2.5 kilotonnes of emissions from the application of a further twelve pesticides has been inventoried in the Canadian portion of the study domain. While suitable data were not available for the U.S. for these twelve additional pesticides, some broad estimates of the total U.S. emissions are provided in Section 11.2.

Table 10.2.7 compares the Ontario emissions of pesticides with emissions for the entire Eastern North America grid. Those pesticides for which U.S. data are not available have been marked with an asterisk to indicate that only emissions from the Canadian areas of the grid are included (see also Section 11.2). The Ontario contributions to emissions are estimated to range from 0.5% for trifluralin to 4.5% for atrazine. These percentages reflect the relative per capita consumption to some extent, but also the types of crop grown, the length of the growing season and other climatological effects which have large effects on Ontario pesticide use.

The top ranking emissions for the entire grid are the herbicides 2,4-D and alachlor, which are predominantly used on field crops such as corn, beans and grains. The top ranking insecticides are carbaryl and carbofuran, both of which are widely used on fruits and vegetables.

Figures 10.2.5 through 10.2.8 show the distribution of pesticide emissions for the entire Eastern North America grid for herbicides, insecticides, fungicides and nematocides. The large production areas for grain, corn and other field crops show a high emission of herbicide (Iowa, Illinois, Kansas, for example), while insecticide emissions correspond largely with the fruit and vegetable growing areas (Michigan, Ohio and the Carolinas, for

example). The areas of intense agriculture in the St. Lawrence river basin are also evident by the emissions of pesticides and herbicides. U.S. data for fungicides and nematocides were not available; hence, only emissions in the Canadian portion of the grid appear on these figures.

In addition, examples that show the hourly output of the modelling emissions preprocessor for the selected species, alachlor and benzo(a)pyrene, are shown on the 33 x 33, 127 km modelling grid for a typical summer weekday for alachlor, and a typical winter day for B(a)P at a selected hour (see Figures 10.2.9 and 10.2.10).

TABLE 10.1.1

Estimated Total Pollutant Class Contributions by General Emission Category for Ontario and Eastern North America

Emission Category		Estimated Annual Emissions (kg)* PAH	PCB	PCDD	PCDF
Industrial	Ontario	82,300		2.44	13.16
	ENA	2,704,000		3.01	14.6
Stationary Fuel Combustion	Ontario	155,000	12.2	2.38	6.24
	ENA	4,545,000	451	72.7	118
Solid Waste Incineration	Ontario	670	1.3	4.19	6.28
	ENA	48,500	42	105	85.6
Transportation	Ontario	24,500		0.041	0.058
	ENA	1,174,000		3.50	4.96
Open Sources	Ontario	9,150	36.9	0.007	0.009
	ENA	926,000	517	2.72	3.85
Total	Ontario	271,600	50.4	9.07	25.7
	ENA	9,397,000	1,010	187	227

* Values after rounding

TABLE 10.1.2

Total Pollutant Annual Emissions in Ontario by Sector

Category/Sector	Estimated Annual Emissions (kg)				
	PAH	PCB	PCDD	PCDF	Pest.
Industrial					
Metallurgical Coke Production	26,218	-	-	-	-
Iron and Steel Production	136	-	-	-	-
Ferrous Foundries	323	-	-	-	-
Ferroalloy Production	53,501	-	-	-	-
Carbon Black Manufacture	380	-	-	-	-
Petroleum Refining	6	-	-	-	-
Asphalt - Roofing Manufacture	7	-	-	-	-
Asphalt - Hot Mix	1,679	-	-	-	-
Kraft Pulping	-	-	0.017	0.009	-
Secondary Copper Production	-	-	2.427	13.155	-
Sub-Total	82,250	-	2.444	13.164	-
Stationary Fuel Combustion					
Electrical Power Generation	8,763	6.83	0.186	0.634	-
Industrial Fuel Combustion	5,609	5.37	0.893	0.443	-
Comm./Inst. Fuel Combustion	393	0.01	-	-	-
Residential Fuel Combustion	461	-	0.000	0.000	-
Residential Fuelwood Combustion	139,804	-	1.302	5.165	-
Sub-Total	155,030	12.21	2.381	6.242	-
Solid Waste Incineration					
Municipal Waste Incineration	520	0.36	4.070	5.908	-
Sewage Sludge Incineration	25	0.88	0.052	0.139	-
Industrial Waste Incineration	71	-	0.058	0.216	-
Comm./Inst. Waste Incineration	49	0.07	0.012	0.012	-
Sub-Total	666	1.31	4.192	6.275	-
Transportation					
On-Road Light Duty Gasoline Vehicles	9,563	-	0.040	0.057	-
On-Road Heavy Duty Gasoline Vehicles	3,306	-	-	-	-
Off-Road Gasoline Vehicles	594	-	0.001	0.001	-
On-Road Diesel Vehicles	10,157	-	-	-	-
Off-Road Diesel Vehicles	831	-	-	-	-
Aircraft	6	-	-	-	-
Railroad	43	-	-	-	-
Marine Vessels	19	-	-	-	-
Sub-Total	24,519	-	0.041	0.058	-
Open Sources					
Forest Fires	849	-	0.001	0.001	-
Prescribed Burning	8,296	-	0.006	0.008	-
Pesticide Use	-	-	-	-	2,703,203
Transformers	-	33.58	-	-	-
Municipal Refuse - Landfill	-	3.27	-	-	-
Sub-Total	9,145	36.85	0.007	0.009	2,703,203
Total	271,610	50.37	9.065	25.748	2,703,203

TABLE 10.1.3

Total PAH Emissions in Ontario for Point, Area and Open Sources and Sector Rank

Category/Sector	Estimated Emissions (kg)			Sector
	Point	Area	Total	Ranking
Industrial				
Metallurgical Coke Production	26,218	-	26,218	3
Iron and Steel Production	136	-	136	20
Ferrous Foundries	323	-	323	19
Ferroalloy Production	53,501	-	53,501	2
Carbon Black Manufacture	380	-	380	18
Petroleum Refining	6	-	6	27
Asphalt - Roofing Manufacture	7	-	7	26
Asphalt - Hot Mix	3	1,676	1,679	10
Sub-Total	80,574	1,676	82,250	
Stationary Fuel Combustion				
Electrical Power Generation	8,763	-	8,763	6
Industrial Fuel Combustion	4,011	142	4,153	8
Comm./Inst. Fuel Combustion	268	125	393	17
Residential Fuel Combustion		461	461	16
Industrial Fuelwood Combustion	1,456	-	1,456	11
Residential Fuelwood Combustion	-	139,804	139,804	1
Sub-Total	14,498	140,532	155,030	
Solid Waste Incineration				
Municipal Waste Incineration	498	22	520	15
Sewage Sludge Incineration	14	11	25	24
Industrial Waste Incineration	71	-	71	21
Industrial Wood Incineration	1	-	1	
Comm./Inst. Waste Incineration	39	10	49	22
Sub-Total	623	43	666	
Transportation				
On-Road Light-Duty Gasoline Vehicles		9,563	9,563	5
On-Road Heavy-Duty Gasoline Vehicles		3,306	3,306	9
Off-Road Gasoline Vehicles		594	594	14
On-Road Diesel Vehicles		10,157	10,157	4
Off-Road Diesel Vehicles		831	831	13
Aircraft		6	6	28
Railroad		43	43	23
Marine Vessels		19	19	25
Sub-Total		24,519	24,519	
Open Sources				
Forest Fires		849	849	12
Prescribed Burning		8,296	8,296	7
Sub-Total		9,145	9,145	
Total	95,695	175,915	271,610	

TABLE 10.1.4

Total PAH Emissions in Ontario for Point, Area and Open Sources and Sector Rank

Category/Sector	Estimated Emissions (kg) Point	Area	Total	Sector Ranking
Stationary Fuel Combustion				
Electrical Power Generation	6.83	-	6.83	2
Industrial Fuel Combustion	5.32	0.05	5.37	3
Commercial Fuel Combustion	0.01	-	0.01	
Sub-Total	12.16	0.05	12.21	
Solid Waste Incineration				
Municipal Waste Incineration	0.36	-	0.36	6
Sewage Sludge Incineration	0.43	0.45	0.88	5
Industrial Waste Incineration	<0.00	-	<0.00	9
Comm./Inst. Waste Incineration	0.06	0.1	0.07	7
Sub-Total	0.85	0.46	1.31	
Open Sources				
Transformers	-	33.58	33.58	1
Municipal Refuse - Landfill	-	3.27	3.27	4
Sub-Total	-	36.85	36.85	
Total	13.01	37.63	50.37	

TABLE 10.1.5

Total PCDD Emissions in Ontario for Point, Area and Open Sources and Sector Rank

Category/Sector	Estimated Emissions (kg) Point	Area	Total	Sector Ranking
Industrial				
Kraft Pulping	0.017	-	0.017	10
Secondary Copper Production	2.427		2.427	2
Sub-Total	2.444	-	2.444	
Stationary Fuel Combustion				
Electric Power Generation	0.186	-	0.186	6
Industrial Fuel Combustion	0.275	0.003	0.278	5
Residential Fuel Combustion	-	0.000	0.000	15
Industrial Fuelwood Combustion	0.615	-	0.615	4
Residential Fuelwood Combustion	-	1.302	1.302	3
Sub-Total	1.076	1.305	2.381	
Solid Waste Incineration				
Municipal Waste Incineration	4.070	-	4.070	1
Sewage Sludge Incineration	0.036	0.016	0.052	8
Industrial Waste Incineration	0.058		0.058	7
Comm./Inst. Waste Incineration	0.010	0.002	0.012	11
Sub-Total	4,174	0.018	4.192	
Transportation				
On-Road Light-Duty Gasoline Vehicles	-	0.040	0.040	9
Off-Road Gasoline Vehicles	-	0.001	0.001	13
Sub-Total	-	0.041	0.041	
Open Sources				
Forest Fires	-	0.001	0.001	14
Prescribed Burning	-	0.006	0.006	12
Municipal Refuse - Landfill	-	0.000	0.000	16
Sub-Total	-	0.007	0.007	
Total	7.694	1.371	9.065	

TABLE 10.1.6

Total PCDF Emissions in Ontario for Point, Area and Open Sources and Sector Rank

Category/Sector	Estimated Emissions (kg) Point	Area	Total	Sector Ranking
Industrial				
Kraft Pulping	0.009	-	0.009	11
Secondary Copper Production	13.155	-	13.155	1
Sub-Total	13.164	-	13.164	
Stationary Fuel Combustion				
Electrical Power Generation	0.634	-	0.634	4
Industrial Fuel Combustion	0.177	0.002	0.179	7
Residential Fuel Combustion	-	0.000	0.000	15
Industrial Fuelwood Combustion	0.264	-	0.264	5
Residential Fuelwood Combustion	-	5.165	5.165	3
Sub-Total	1.075	5.167	6.242	
Solid Waste Incineration				
Municipal Waste Incineration	5.908	-	5.908	2
Sewage Sludge Incineration	0.083	0.056	0.139	8
Industrial Waste Incineration	0.216	-	0.216	6
Comm./Inst. Waste Incineration	0.010	0.002	0.012	10
Sub-Total	6.217	0.058	6.275	
Transportation				
On-Road Light-Duty Gasoline Vehicles	-	0.057	0.057	9
Off-Road Gasoline Vehicles	-	0.001	0.001	13
Sub-Total	-	0.058	0.058	
Open Sources				
Forest Fires	-	0.001	0.001	14
Prescribed Burning	-	0.008	0.008	12
Sub-Total	-	0.009	0.009	
Total	20.456	5.292	25.748	

TABLE 10.1.7

Speciated Toxic Chemical Emission Totals in Ontario

Compound	Estimated Emissions (kg)
PAH Compound	
Acenaphthene	6,291
Acenaphthylene	27,834
Anthracene	16,011
Benz(a)anthracene	6,171
Benzofluoranthenes	19,906
Benzo(b)fluoranthene	477
Benzo(j)fluoranthene	-
Benzo(k)fluoranthene	25
Benzo(a)fluorene	1,299
Benzo(ghi)perylene	5,936
Benzo(a)pyrene	5,086
Benzo(e)pyrene	1,219
Carbazole	470
Chrysene	8,375
Coronene	656
Cyclopenta(cd)pyrene	7,758
Dibenz(ah)acridine	-
Dibenz(ah)anthracene	314
7h-Dibenzo(cg)carbazole	22
Dibenzo(def,mno)chrysene	-
Dibenzothiophene	103
Fluoranthene	27,379
Fluorene	33,723
Indeno(1,2,3-cd)pyrene	2,626
Methylanthracenes	15,794
Methylphenanthrenes	25,329
1-Nitropyrene	79
Perylene	1,173
Phenanthrene	29,334
Pyrene	28,050
Triphenylene	156
Total	**271,599**

TABLE 10.1.7 (Cont'd.)

Speciated Toxic Chemical Emission Totals in Ontario

Compound	Estimated Emissions (kg)
PCB Congener	
Total PCB	**50.37**
PCDD Congener	
$2378T_4CDD$	.057
T_4CDD	1.251
P_5CDD	1.795
H_6CDD	2.360
H_7CDD	2.290
OCDD	1.035
PCDD	0.278
Total	**9.066**
PCDF Congener	
$2378T_4CDF$	1.237
T_4CDF	9.111
P_5CDF	7.123
H_6CDF	4.558
H_7CDF	2.301
OCDF	1.239
PCDF	0.180
Total	**25.749**
Herbicides	
Alachlor	195,158
Atrazine	220,707
Butylate	8,954
Cyanazine	60,023
2,4-D	184,831
Linuron	99,847
Metolachlor	156,900
Metribuzin	51,511
MPCA	52,445
Trifluralin	9,521
Total	**1,039,897**

TABLE 10.1.7 (Cont'd.)

Speciated Toxic Chemical Emission Totals in Ontario

Compound	Estimated Emissions (kg)
Insecticides	
Carbaryl	19,648
Carbofuran	7,409
Chlordane	354
Diazinon	8,580
Endosulfan	7,298
Lindane	2
Methoxychlor	1,388
Total	**44,679**
Fungicides	
Captan	78,028
Total	**78,028**
Nematocides	
Chloropicrin	58,436
Dichloropropenes/Propanes	1,296,329
Methylisothiocyanate	185,800
Total	**1,540,565**

TABLE 10.2.1

Total Pollutant Annual Emissions by Sector for ENA

Category/Sector	Estimated Emissions (kg) PAH	PCB	PCDD	PCDF	Pest.
Industrial					
Metallurgical Coke Production	146,042	-	-	-	-
Iron and Steel Production	883	-	-	-	-
Ferrous Foundries	11,232	-	-	-	-
Ferroalloy Production	943,606	-	-	-	-
Primary Aluminum Production	1,590,883	-	-	-	-
Carbon Black Manufacture	3,158	-	-	-	-
Wood Charcoal Production	1,156	-	-	-	-
Petroleum Refining	325	-	-	-	-
Asphalt - Roofing	370	-	-	-	-
Asphalt - Hot Mix	5,933	-	-	-	-
Kraft Pulping	-	-	0.351	0.193	-
Secondary Copper	-	-	2.66	14.44	-
Sub-Total	2,703,588	-	3.011	14.633	-
Stationary Fuel Combustion					
Electrical Power Generation	95,834	337.61	9.222	31.364	-
Industrial Fuel Combustion	1,063,908	113.44	5.861	3.781	-
Comm./Inst. Fuel Combustion	120,862	-	-	-	-
Residential Fuel Combustion	162,050	-	0.584	1.852	-
Residential Fuelwood Combustion	2,921,640	-	27.499	68.022	-
Industrial Wood Combustion	179,601	-	29.555	12.666	-
Stationary Internal Combustion	854	-	-	-	-
Sub-Total	4,544,749	451.05	72.721	685	-
Solid Waste Incineration					
Municipal Waste Incineration	7,458	11.13	25.443	30.219	-
Sewage Sludge Incineration	90	3.68	0.151	0.486	-
Industrial Waste Incineration	37,425	6.84	78.154	51.064	-
Comm./Inst. Waste Incineration	3,538	3.02	1.592	3.858	-
Waste Oil Combustion	11	16.97	-	-	-
Sub-Total	48,522	41.64	105.340	85.627	-

TABLE 10.2.1 (Cont'd.)

Total Pollutant Annual Emissions by Sector for ENA

Category/Sector	Estimated Emissions (kg) PAH	PCB	PCDD	PCDF	Pest.
Transportation					
On-Road Light-Duty Gasoline Vehicles	579,448	-	3.172	4.489	-
On-Road Heavy-Duty Gasoline Vehicles	129,698	-	0.191	0.270	-
Off-Road Gasoline Vehicles	64,643	-	0.098	0.138	-
On-Road Diesel Vehicles	284,803	-	-	-	-
Off-Road Diesel Vehicles	71,953	-	-	-	-
Aircraft	5,038	-	-	-	-
Railroad	3,941	-	-	-	-
Marine Vessels	34,122	-	0.044	0.062	-
Sub-Total	1,173,635	-	3.505	4.959	-
Open Sources					
Res./Indus./Comm. On-Site Burning	11,779	-	-	-	-
Res./Indus./Comm. On-Site Incineration	10,175	8.24	1.918	2.829	-
Forest Fires	226,641	-	0.177	0.224	-
Prescribed Burning	677,579	-	0.629	0.796	-
Pesticide Use	-	-	-	-	34,450,292
Transformers	-	440.47	-	-	-
Municipal Refuse - Landfill	0	68.73	-	-	-
Sub-Total	926,174	517.44	2.724	3.849	34,450,292
Overall Total	9,396,668	1,010.13	187.301	226.753	34,450,292

TABLE 10.2.2

Important Contributing Sectors by Pollutant Class

Relative Source Strength Rank	Pollutant Class	Ontario	ENA
1	PAH	Residential Wood Comb.	Residential Wood Comb.
2		Ferroalloy Production	Primary Aluminum Prod.
3		Metallurgical Coke Prod.	Industrial Fuel Comb.
4		On-Road Diesel Vehicles	Ferroalloy Prod.
5		Light-Duty Gasoline Vehicles	Prescribed Burning
1	PCB	Transformer Leakage	Transformer Leakage
2		Electric Power Generation	Electric Power Generation
3		Industrial Fuel Comb.	Industrial Fuel Comb.
4		Landfills	Landfills
5		Sewage Sludge Incin.	Waste Oil Comb.
1	PCDD	Municipal Waste Incin.	Industrial Waste Incin.
2		Secondary Copper Prod.	Industrial Wood Comb.
3		Residential Wood Comb.	Residential Wood Comb.
4		Industrial Fuel Comb.	Municipal Waste Incin.
5		Electric Power Generation	Electric Power Generation
1	PCDF	Secondary Copper Prod.	Residential Wood Comb.
2		Municipal Waste Incin.	Industrial Waste Incin.
3		Residential Fuelwood Comb.	Electric Power Generation
4		Electric Power Generation	Municipal Waste Incin.
5		Sewage Sludge Incin.	Industrial Wood Comb.

TABLE 10.2.3

Toxic Chemical Emissions for Point, Area and Open Sources by Emission Category in Eastern North America

Emission Category	Total Emissions (kg) Ontario Point	Ontario Area	Canada (less Ont.) Point	Canada (less Ont.) Area	U.S. Point	U.S. Area
PAH						
Industrial	80,574	1,676	811,577	4,096	1,805,675	
Stationary Fuel Combustion	14,498	140,532	2,487	426,404	1,356,269	2,604,586
Solid Waste Incineration	623	43	1,369	28,029	18,460	
Transportation		24,519		43,466		1,105,653
Open Sources		9,145		482,952	4	434,072
PCB						
Industrial						
Stationary Fuel Combustion	12.16	0.05	3.27	0.70	420.51	14.37
Solid Waste Incineration	0.85	0.46	2.12		38.19	
Transportation						
Open Sources		36.85		27.42		453.16
PCDD						
Industrial	2.444		0.036		0.535	
Stationary Fuel Combustion	1.076	1.305	0.090	3.899	42.613	23.738
Solid Waste Incineration	4.174	0.018	4.216	0.699	96.232	
Transportation		0.041		0.098		3.366
Open Sources		0.007		0.377		2.340
PCDF						
Industrial	13.164		0.020		1.447	
Stationary Fuel Combustion	1.075	5.167	0.304	12.939	45.896	52.305
Solid Waste Incineration	6.217	0.058	4.796	2.590	71.964	
Transportation		0.058		0.138		4.764
Open Sources		0.009		0.476		3.364

TABLE 10.2.4

Comparison of U.S. Emission Estimates for PAH[1]

Emission Sectors	U.S. Estimated PAH Emissions (Tonnes)			
	A. Little (1978)[2]	Ramdahl (1978)[2]	Peters (1981)[2]	Partial U.S. Estimate for This Study[3]
	8,368	8,422	11,031	7,325
	Category Contribution (%)			
Industrial				
- Coke Ovens	<1	7	6	2
- Aluminum Smelters	-	25	-	13
- Other	2	-	-	10
Stationary Fuel Comb.				
- Utility Boilers	1	5	1	1
- Residential Wood	58	45	35	32
- Residential Coal	10	1	1	1
- Other	-	-	-	19
Transportation	3	3	20	15
Waste Incineration	-	-	-	<1
Open Burning	24	12	35	6

Notes: 1. Tabulated data for other U.S. studies cited in NRCC 1983, Dann 1989.

2. Estimates for the entire U.S. emissions conducted for mid to late 1970's (unknown PAH species).

3. Current estimate for Eastern U.S. States (representing ~70% of total U.S.criteria pollutant emissions). Data exclude naphthalene.

TABLE 10.2.5

Speciated Toxic Chemical Emission Totals in Eastern North America

Compound	Estimated Emissions (kg)
PAH Compound	
Acenaphthene	143,626
Acenaphthylene	672,111
Anthracene	914,066
Benz(a)anthracene	339,180
Benzofluoranthenes	559,826
Benzo(b)fluoranthene	8,149
Benzo(j)fluoranthene	-
Benzo(k)fluoranthene	922
Benzo(a)fluorene	48,119
Benzo(ghi)perylene	251,232
Benzo(a)pyrene	340,165
Benzo(e)pyrene	118,419
Carbazole	3,859
Chrysene	353,954
Coronene	22,761
Cyclopenta(cd)pyrene	139,519
Dibenz(ah)acridine	5
Dibenz(ah)anthracene	20,817
7h-Dibenzo(cg)carbazole	79
Dibenzo(def,mno)chrysene	67
Dibenzothiophene	628
Fluoranthene	1,391,292
Fluorene	692,691
Indeno(1,2,3-cd)pyrene	98,734
Methylanthracenes	401,258
Methylphenanthrenes	568,011
1-Nitropyrene	2,816
Perylene	16,187
Phenanthrene	683,401
Pyrene	1,598,597
Triphenylene	5,024
PAH	1,156
Total	9,396,670

TABLE 10.2.5 (Cont'd.)

Speciated Toxic Chemical Emission Totals in Eastern North America

Compound	Estimated Emissions (kg)
PCB Congener	
Total PCB	**1,010.1**
PCDD Congener	
2378T_4CDD	.721
T_4CDD	42.537
P_5CDD	53.087
H_6CDD	52.194
H_7CDD	23.061
OCDD	9.842
PCDD	5.862
Total	**187.304**
PCDF Congener	
2378T_4CDF	4.661
T_4CDF	55.935
P_5CDF	69.849
H_6CDF	48.006
H_7CDF	19.763
OCDF	4.757
PCDF	3.782
Total	**226.752**
Herbicides	
Alachlor	7,242,584
Atrazine	4,873,500
Butylate	13,146*
Cyanazine	1,533,653
2,4-D	10,692,160
Linuron	108,735*
Metolachlor	3,645,907
Metribuzin	58,940*
MPCA	568,213*
Trifluralin	2,058,262
Total	**30,795,100**

TABLE 10.2.5 (Cont'd.)

Speciated Toxic Chemical Emission Totals in Eastern North America

Compound	Estimated Emissions (kg)
Insecticides	
Carbaryl	1,871,729
Carbofuran	982,727
Chlordane	853*
Diazinon	219,647
Endosulfan	11,294*
Lindane	2,566*
Methoxychlor	2,114*
Total	**3,090,930**
Fungicides	
Captan	132,276*
Total	**132,276**
Nematocides	
Chloropicrin	59,768*
Dichloropropenes/Propanes	1,330,088*
Methylisothiocyanate	185,800
Total	**1,575,656**

* U.S. data not available (see Section 11.2)

TABLE 10.2.6

Comparison of Speciated PAH Totals from Emission Inventories and Ambient Concentration Data

PAH Compound	Estimated PAH Emissions (tonnes) NAPAP[1]	Current[2] ENA	Current[2] Ont.	Mean Toronto Ambient Air Conc. 1984-86 (ng/m^3)[3]
Acenaphthene	2.5	144	6.3	2.24[5]
Acenaphthylene	311	672	27.8	4.12[5]
Anthracene	31[4]	914	16.0	1.60
Anthanthrene	-	-	-	0.02
Benz(a)anthracene	0.7[4]	339	6.2	0.4
Benzo(b)chrysene	-	-	-	0.04
Benzo(b)fluoranthenes	0	560	0.5	
Benzo(b+k)fluoranthene	0			1.26
Benzo(ghi)fluoranthene	0	-	-	0.49
Benzo(a)fluorene	-	48	1.3	0.53
Benzo(b)fluorene	-	-	-	0.27
Benzo(ghi)perylene	-	251	5.9	0.77
Benzo(a)pyrene	0.5[4]	340	5.1	0.30
Benzo(e)pyrene	-	118	1.2	0.48
Carbazole	-	3.9	0.5	-
Chrysene	135	354	8.4	
Chrysene and Triphenylene	-			0.73
Coronene	-	23	0.7	-
Cyclopenta(cd)pyrene	-	140	7.8	-
Dibenz(ah)acridine	-	<0.1	-	-
Dibenz(ah)anthracene	-	21	0.3	
Dibenz(ac)+(ah) anthracene	-			0.04
7H-Dibenz(cg)carbazole	-	<0.1	0.02	-
Dibenzo(def,mno)chrysene	-	<0.1	-	-
Dibenzothiophene	-	0.6	0.1	-
Fluoranthene	150	1,391	27.4	4.91
Fluorene	149	693	33.7	5.51[5]
Indeno(1,2,3-cd)pyrene	-	99	2.6	0.46
Methylanthracenes	-	401	15.8	-
Methylphenanthrenes	-	568	25.3	-
7-Methyl-Benz(a)anthracene	-	-	-	0
2-Methyl-Cholanthrene	-	-	-	0.02
2-Methyl-Fluorene	-	-	-	3.6
1-Methyl-Pyrene	-	-	-	0.18
1-Nitropyrene	-	2.8	0.08	
Perylene	-	16	1.2	0.04
Phenanthrene	8838	683	29.3	15.64
Pyrene	146	1,599	28.1	3.87
Triphenylene	-	5.0	0.2	
Total	1,764	9,397	271.6	47.57

TABLE 10.2.6 (Contd.)

Comparison of Speciated PAH Totals from Emission Inventories and Ambient Concentration Data

Notes:
1. Emission species tabulated in the 1985 NAPAP Inventory. Although emission units were not specified, tonnes are presumed (U.S. EPA 1989b). PAH emissions may be based mainly (or entirely) on residential wood burning and aluminum smelting data.
2. Emission estimates in this study for Eastern North America.
3. Seasonal ambient air particulate and vapour concentrations (mean of 42 samples) measured at an urban site in Toronto during 1984-86 (Dann 1989).
4. Particle phase emissions only.
5. Sample collection efficiency reported to be poor and dependent on ambient temperature.

TABLE 10.2.7

Estimated Speciated Pesticide Emissions in Ontario and Eastern North America

	Estimated Emissions (kg)* Ontario	ENA
Herbicides		
Alachlor	195,200	7,243,000
Atrazine	220,700	4,874,000
Butylate	8,950	13,200**
Cyanazine	60,000	1,534,000
2,4-D	184,800	10,691,000
Linuron	99,900	108,700**
Metolachlor	156,900	3,646,000
Metrabuzin	51,500	58,900**
MCPA	52,400	568,200**
Trifluralin	9,520	2,058,000
Total	1,039,900	30,795,000
Insecticides		
Carbaryl	19,650	1,872,000
Carbofuran	7,410	982,700
Chlordane	354	853**
Diazinon	8,580	219,600
Endosulfan	7,300	11,300**
Lindane	2	2,570**
Methoxychlor	1,390	2,110**
Total	44,680	3,091,000
Fungicides		
Captan	78,030	132,300**
Nematocides		
Chloropicrin	58,400	59,800**
Dichloropropenes/propanes	1,296,300	1,330,100**
Methylisothiocyanate	185,800	185,800**
Total	1,540,500	1,575,700

* Values after rounding
** Data not available in the U.S.

Figure 10.1.1

Annual Emissions of PAH (Point and Area) in Southern Ontario

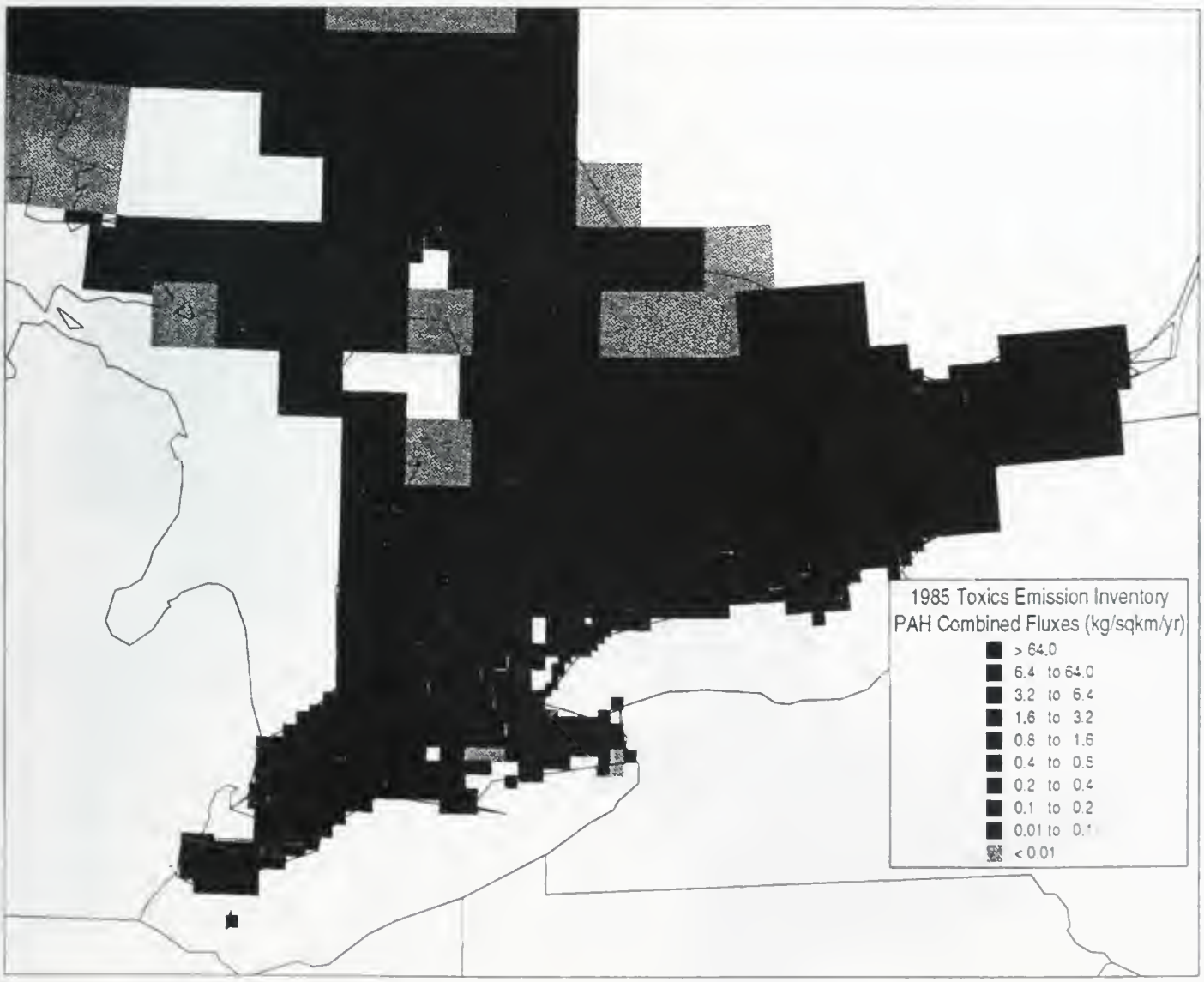


Figure 10.1.2

Annual Emissions of PAH (Point and Area) in Ontario

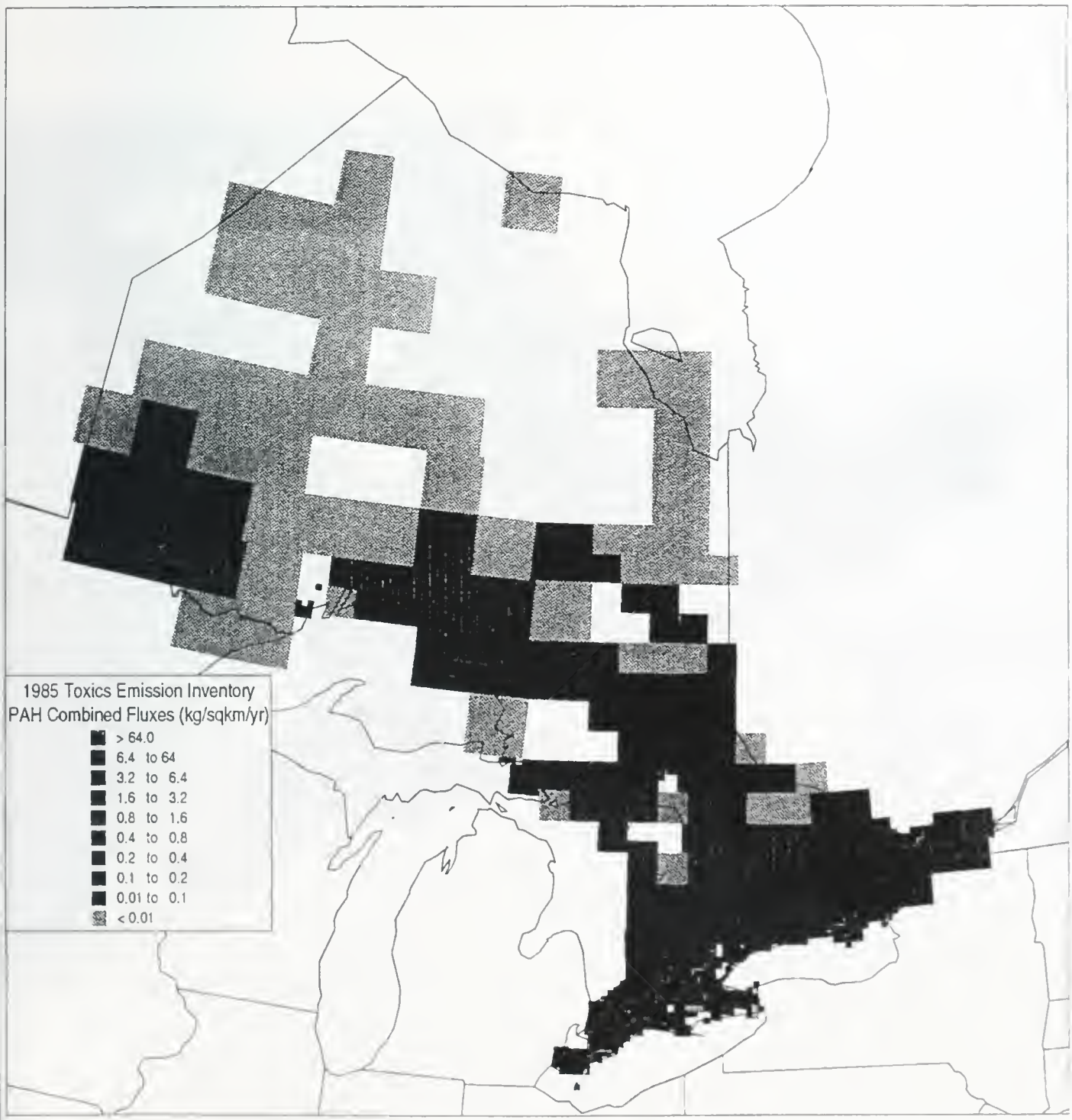


Figure 10.1.3

Annual Emissions of PCB (Point and Area) in Southern Ontario

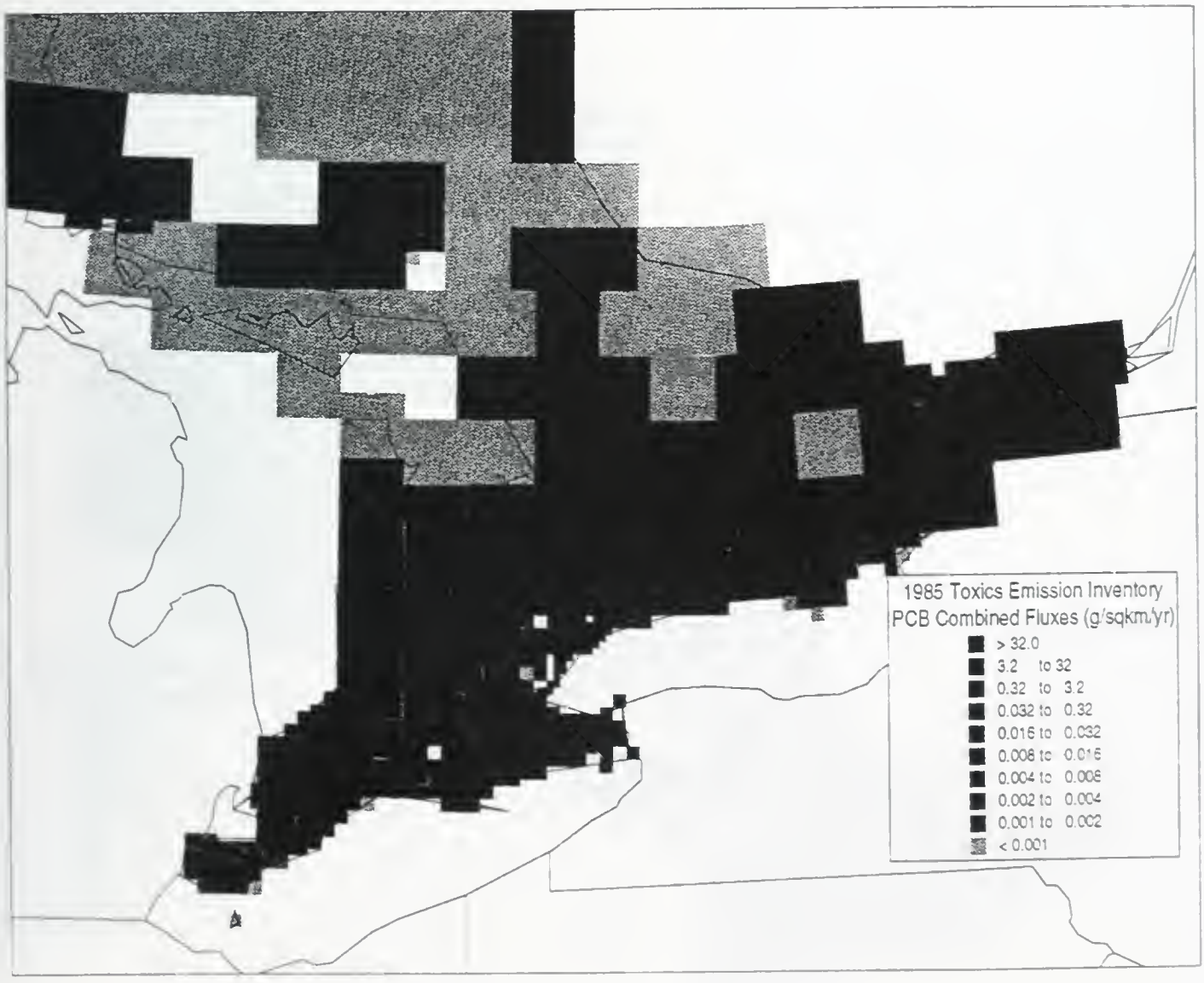


Figure 10.1.4

Annual Emissions of PCB (Point and Area) in Ontario

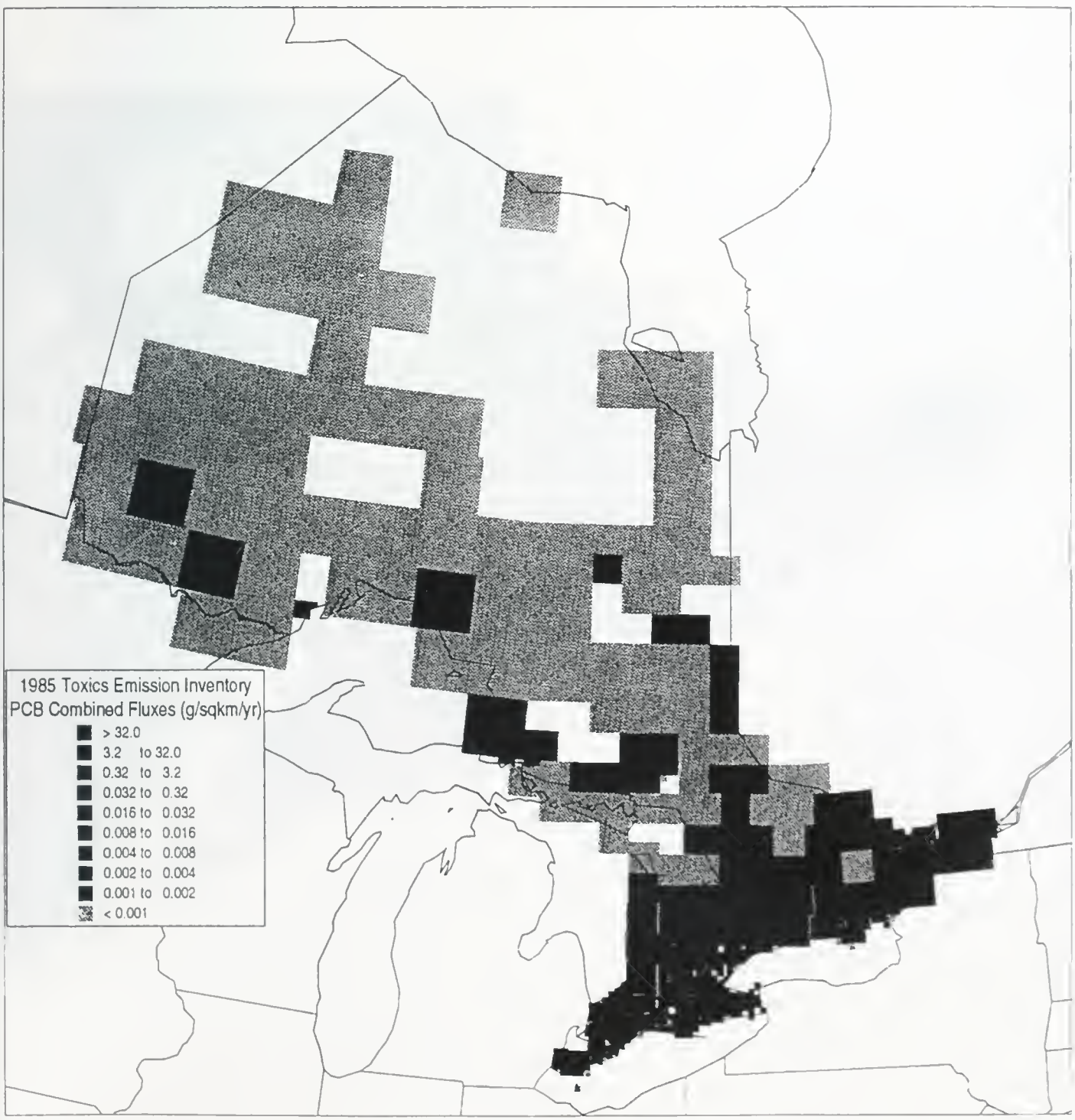


Figure 10.1.5

Annual Emissions of PCDD (Point and Area) in Southern Ontario

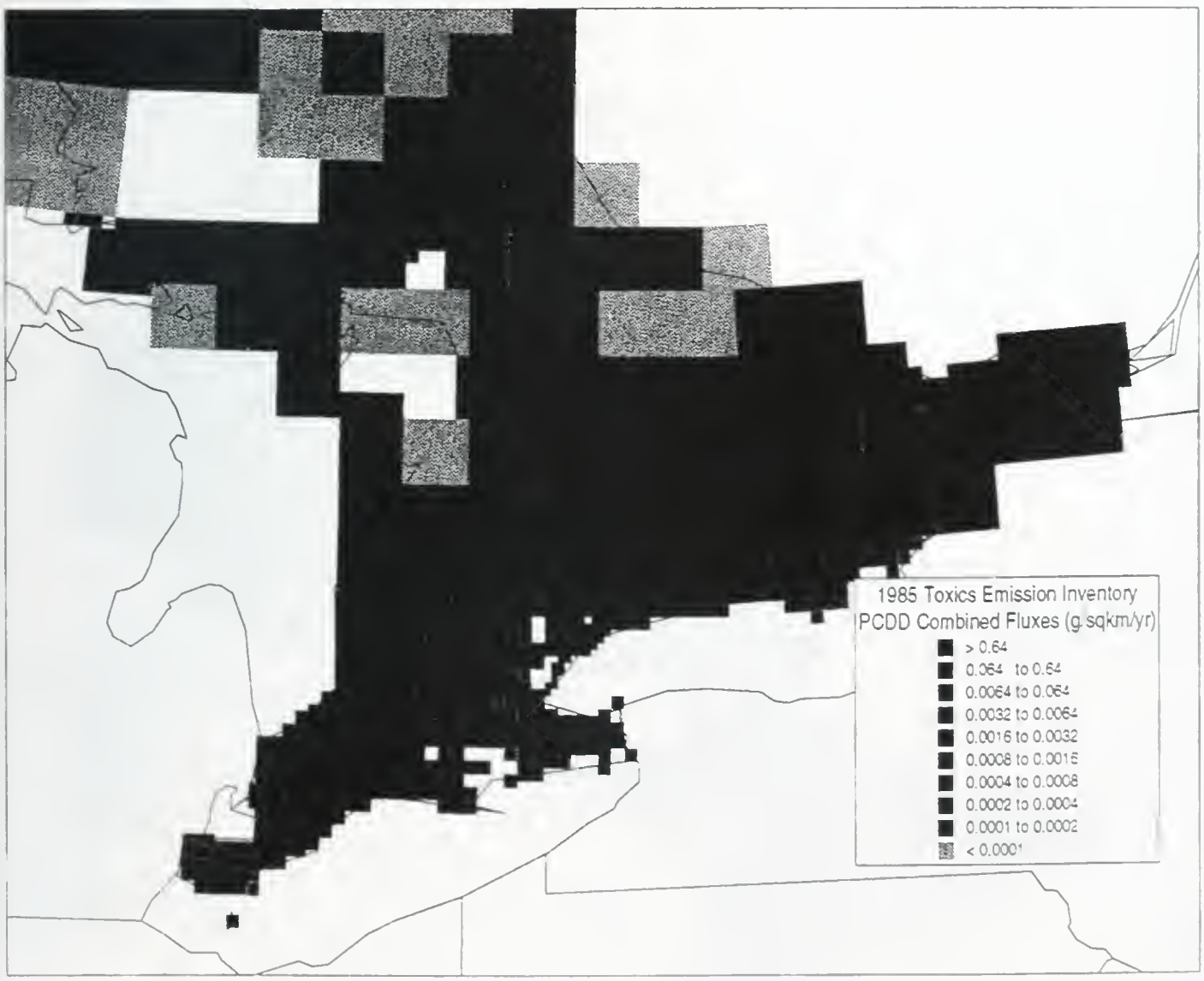


Figure 10.1.6

Annual Emissions of PCDD (Point and Area) in Ontario

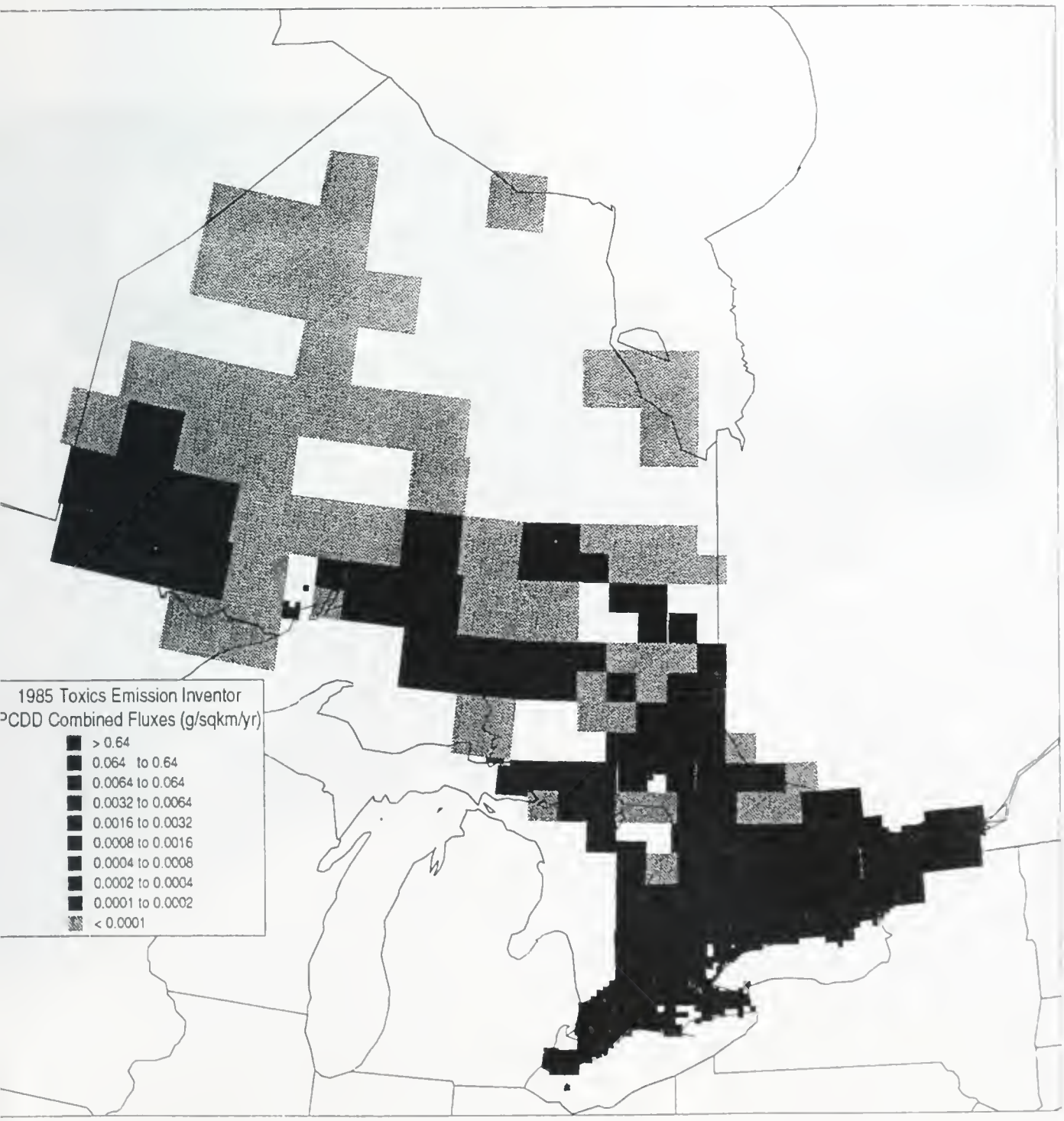


Figure 10.1.7

Annual Emissions of PCDF (Point and Area) in Southern Ontario

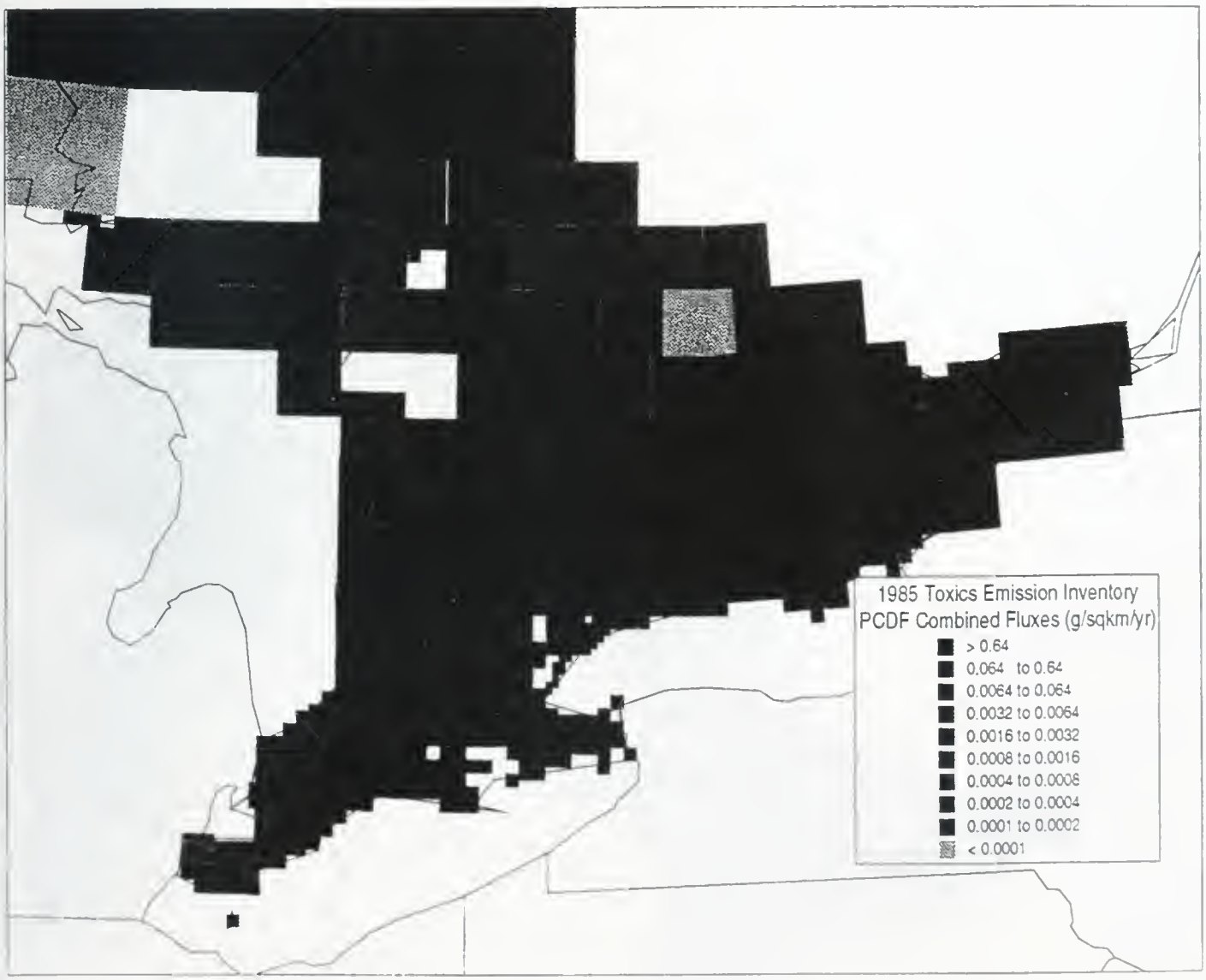


Figure 10.1.8

Annual Emissions of PCDF (Point and Area) in Ontario

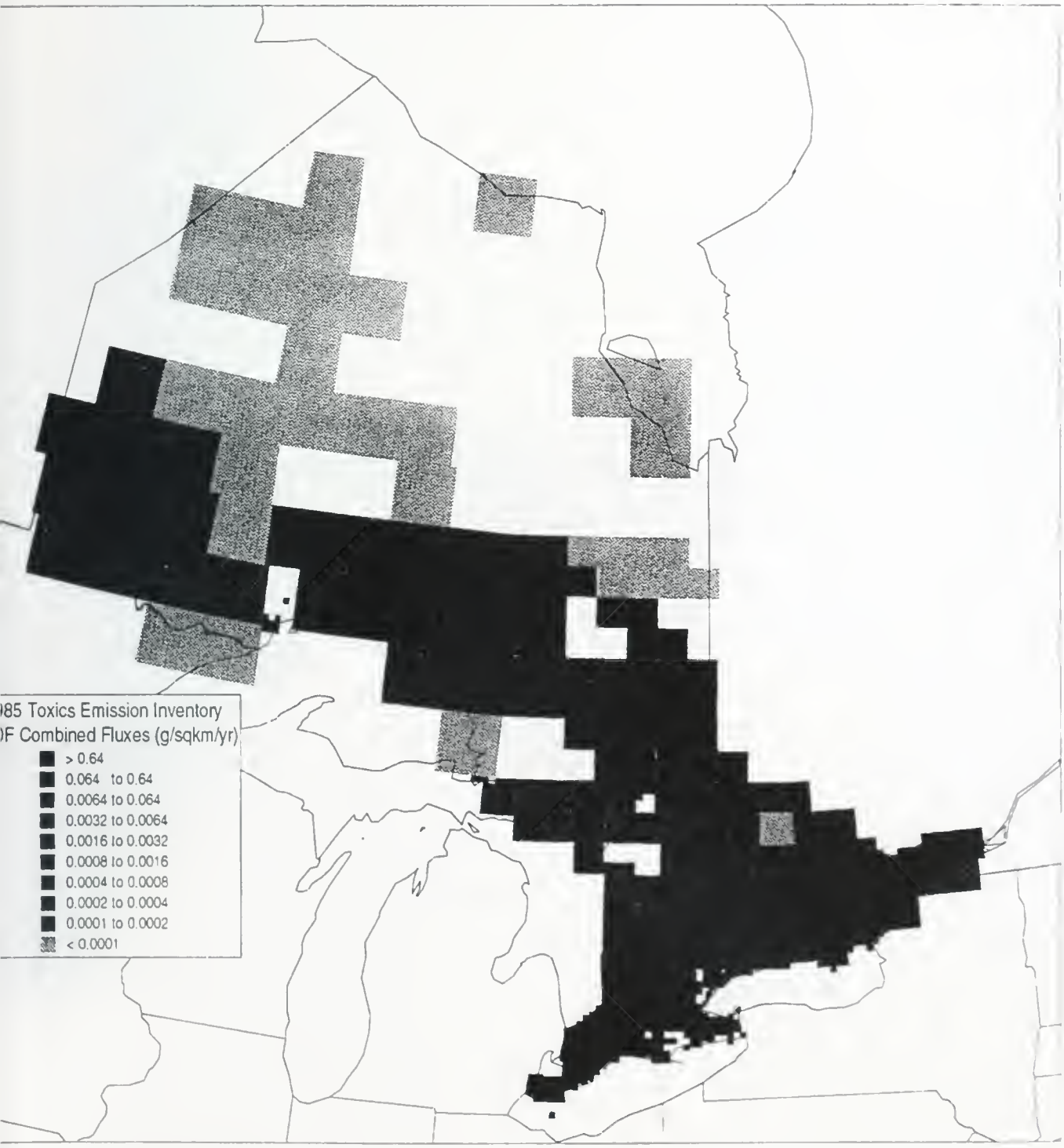


Figure 10.1.10

Annual Emissions of Insecticides in Ontario

Figure 10.1.12

Annual Emissions of Nematocide in Ontario

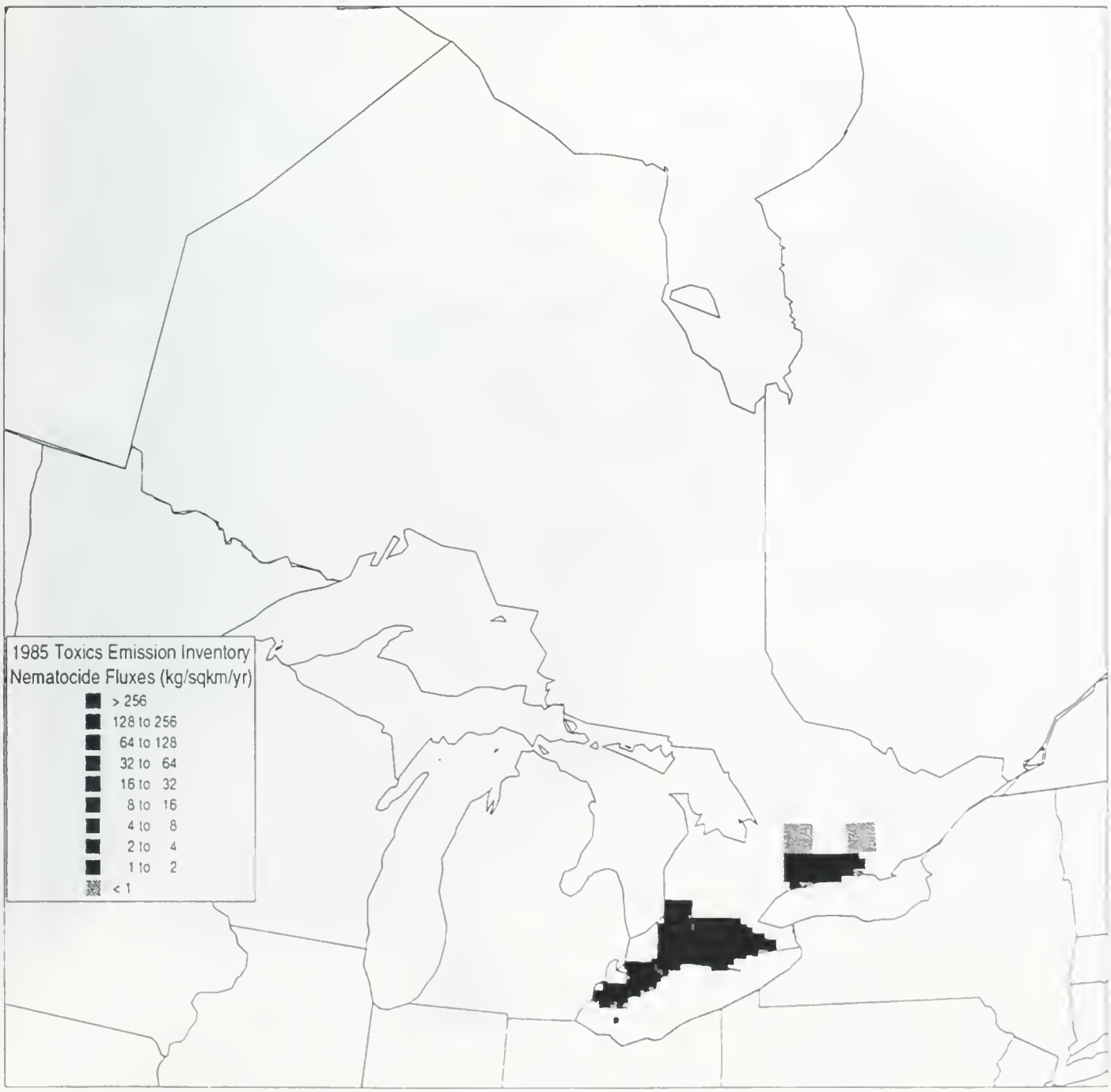


Figure 10.2.1

Annual Emissions of PAH (Point and Area) in Eastern North America

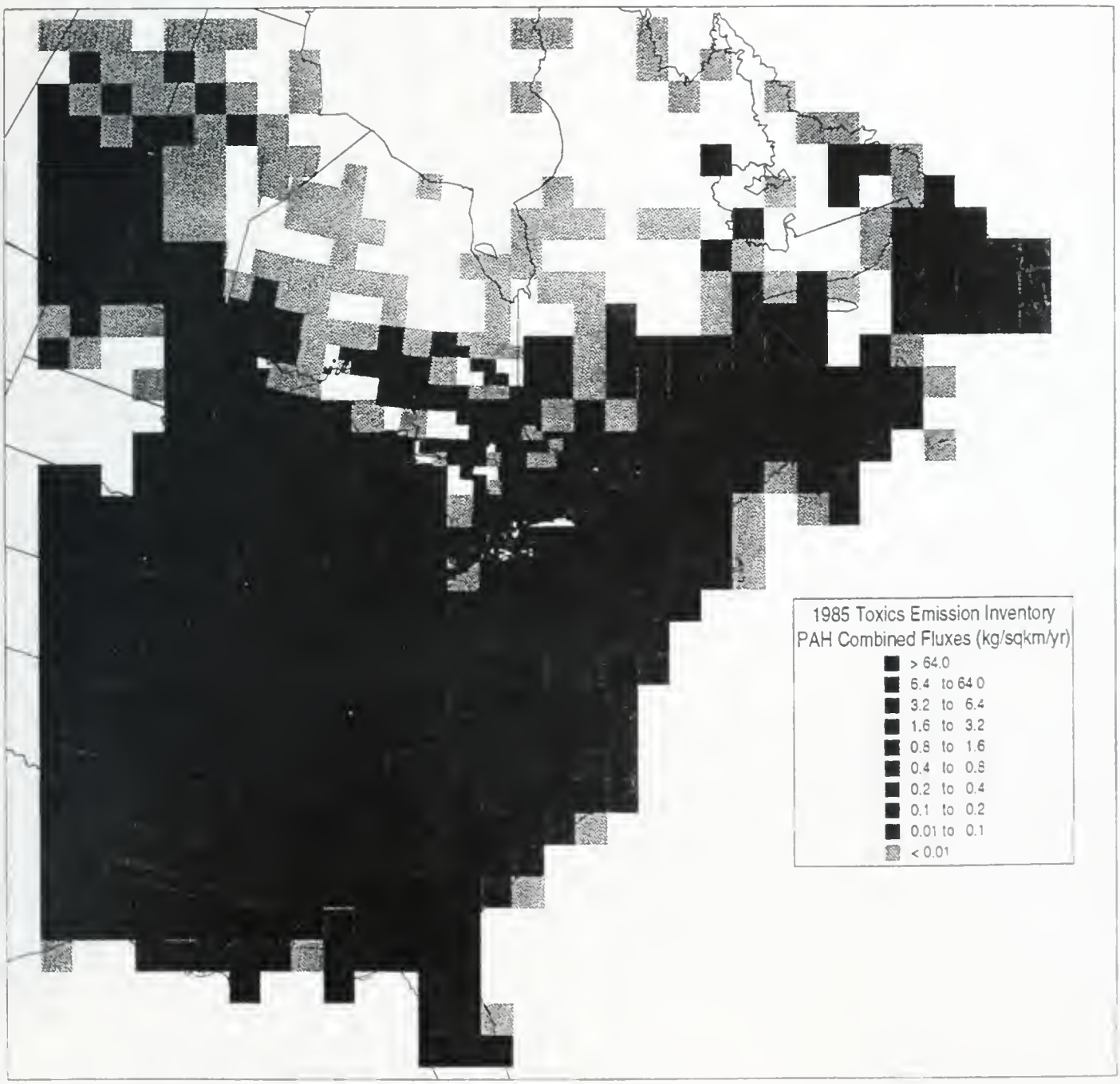


Figure 10.2.2

Annual Emissions of PCB (Point and Area) in Eastern North America

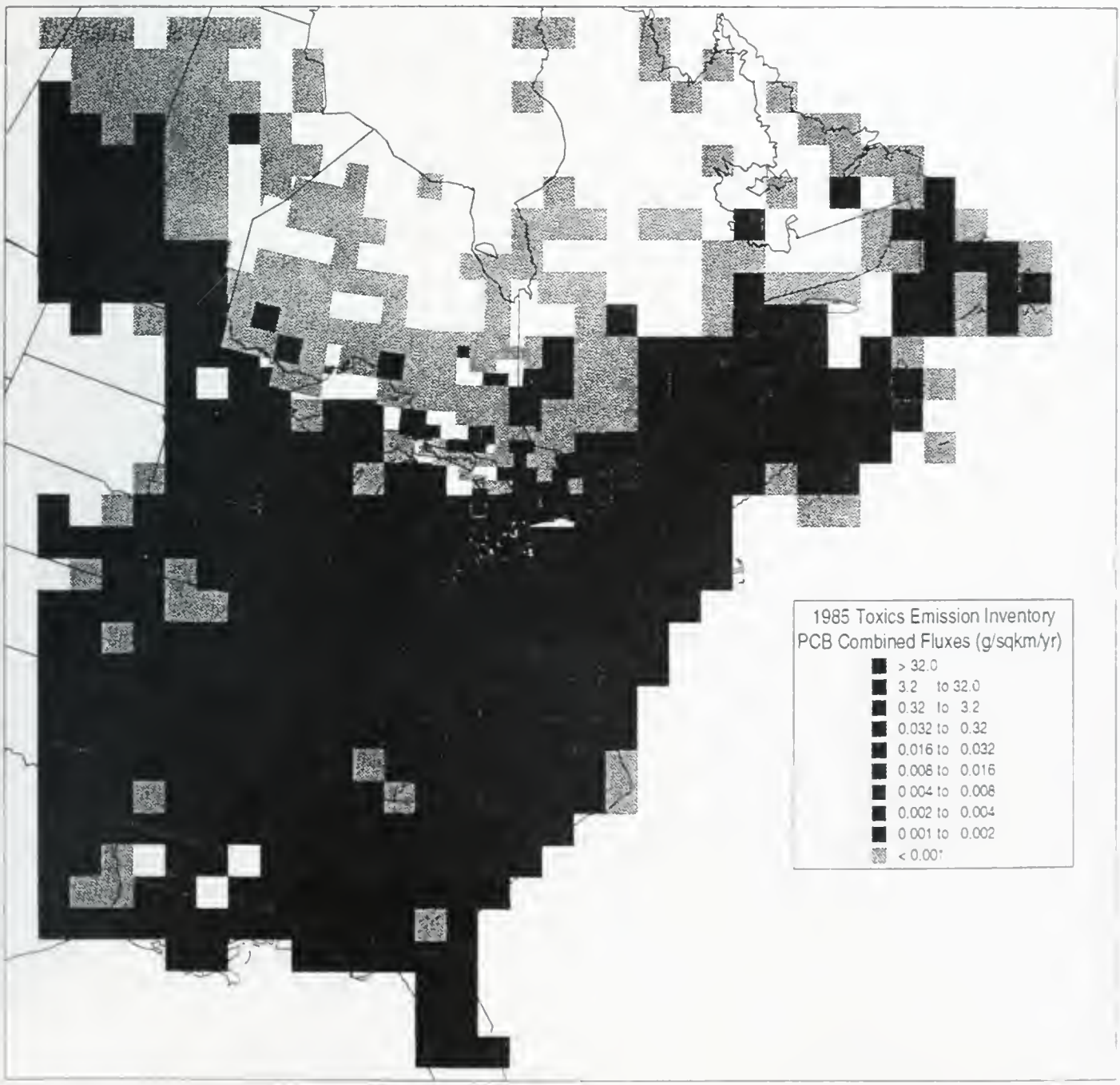


Figure 10.2.3

Annual Emissions of PCDD (Point and Area) in
Eastern North America

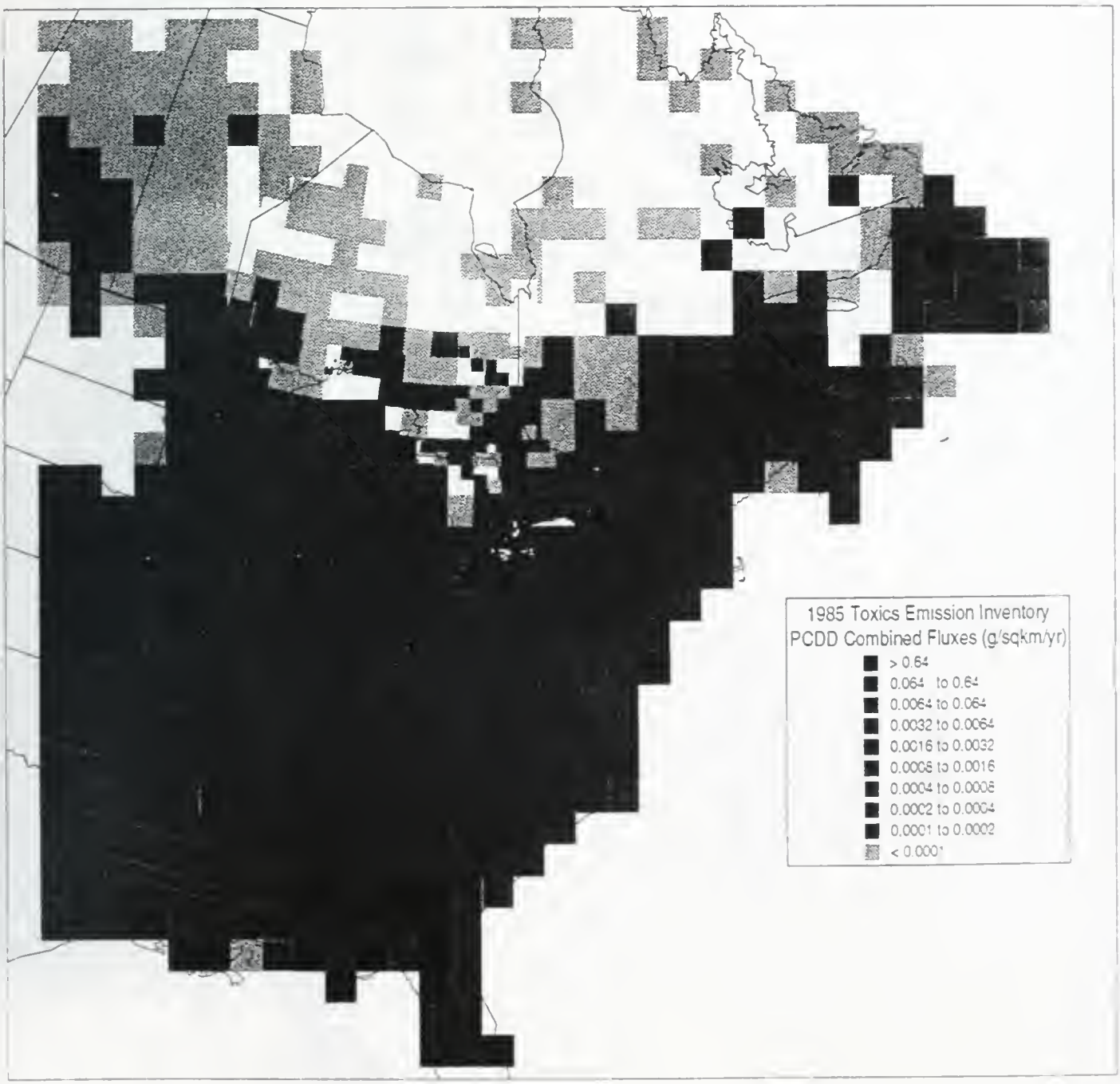
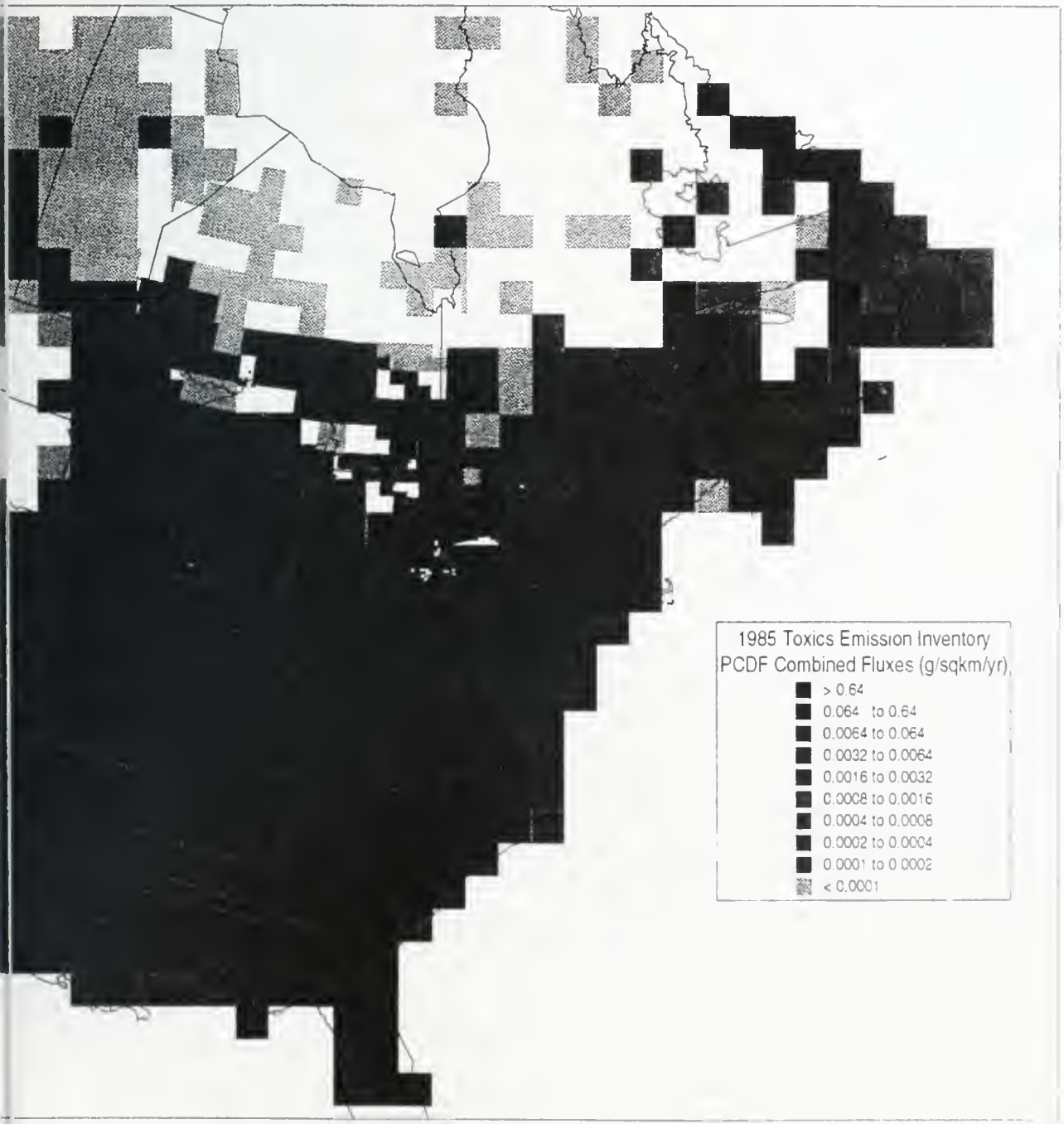


Figure 10.2.4

Annual Emissions of PCDF (Point and Area) in Eastern North America



11. DISCUSSION OF INVENTORY LIMITATIONS

Several inventory limitations have been noted in Section 3.11 and in various sector descriptions of the report pertaining to methods of preparing the inventory, compound classifications, as well as both limited amount and variability of data. This discussion focuses primarily on limitations pertaining to the inventory results, in order to provide a further perspective of the reported data and assist in future compilations.

11.1 Data Availability

Reasonably accurate emission inventories and databases have been developed in recent years for criteria pollutant emissions of traditional contributing sources, whereby large-scale regional models can be applied in an effort to quantify emission impacts at various receptors. Rather than assembling fundamental inventory information, it was useful in this study to utilize available traditional source information that has been compiled at the SCC level, quality assured, and spatially and temporally resolved in the most recent NAPAP inventory. Thus, for the grid area in Eastern North America, it was particularly beneficial to select and assimilate base quantity and other data in the NAPAP files that were pertinent to the sources and processes examined in this study (e.g., some industrial sources and much of the data for other general source categories of stationary fuel combustion, transportation, etc.). Specific errors or omissions might have occurred during extraction of the data, especially for Canadian sources in which some SCC codes at the process level have been assigned without a descriptor. It is apparent that a portion of the Canadian primary aluminum emissions may not have been included in the present study as a result of this or other possible reasons (see Section 10.2). Similarly, a portion of some expected Canadian area source fuel contributions may be somewhat incomplete after back-calculating from criteria pollutant emissions data (see Section 3.6). Most of the traditional source base quantity data have been , however, accounted for in this study.

Several other non-traditional types of sources considered relevant to the toxics inventory were not contained in the NAPAP criteria pollutant inventory and associated data required derivation of estimation (e.g., certain industrial and incineration sources and several open sources, particularly pesticides). There were also a few specific Canadian source sectors with expected contributions that were missing in the NAPAP and other databases, but have been inventoried in the U.S. Potential sources of this type in Ontario are

noted in Section 11.2 (e.g., certain types of incinerators and specific open burning sources). Such missing sources are recognized to contribute only small amounts of criteria pollutant emissions relative to other sources, but can be relatively stronger sources of some toxic chemicals. In addition, there are other potential types of toxic chemical sources for which relevant information or inventory data (e.g., base quantities, emission factors, locations) are either extremely limited or unavailable (see Section 11.2). For some of these chemical classes and non-traditional sources, as noted in other sections of the report, there were no (or limited) precedent inventories to provide guidance on the strength of various sources or to compare emission estimates that have been made as a check on the current data quality or completeness.

The estimation of pesticide emissions was particularly difficult in terms of the data available on which the base spatially and temporally resolved emissions. Pesticide use or sales data for many pesticides are considered highly confidential by the producers and, even where such data must be disclosed to government departments, disclosure is made on a strictly confidential basis. As a result, pesticide application data are based on limited published survey data carried out provincially or by state. The spatial distribution of these data is then done by crop type. In the U.S., a recent inventory of 25 selected pesticides was available which included nine pesticides which were of interest to this study. Some of the available data for pesticide use were reported in terms of the generic compound type without speciation into the individual compounds, and special methods had to be developed to speciate these groups. While the year 1985 was the targeted base-year for this inventory, the use of data for other years ranging from 1982 had to be resorted to in view of the sparseness of published pesticide data.

11.2 Data Gaps

Base quantity or production rate data were lacking or insufficient to include various toxic chemical emissions in the inventory database for some potential or suspected sources in Ontario and other Canadian provinces. Although, in some instances, emission factors were developed and applied to similar sources in the U.S., the lack of base quantity data and uncertainty of the extent to which such sources exist in Ontario, precluded the use of corresponding estimated emissions in the database. Instead, a rough estimate of potential emissions from such sources was done (see Table 11.2.1), in order to provide an indication of the emission strengths. For several of these potential source sectors it was assumed that the emissions were equivalent to 5% of the total Eastern U.S. emissions by sector on the basis of a roughly-estimated population ratio between Ontario and the Eastern Unites States. Very limited data have been found on amounts of wastes incinerated or burned by industries, institutions, apartment buildings and at non-urbanized residences. Due to the various assumptions and specific reported information that were used to estimate three possible emissions, it is expected that the estimates will have a high level of uncertainty. For example, small amounts of PCDD emissions have been reported in some cement kiln stack measurements that might be related to combustion of the primary kiln fuels (such as coal or coke which is assigned to the industrial fuel combustion sector) and waste solvents used as fuel supplements. However, information regarding the extent of fuel supplement usage (e.g., waste solvents or waste oils) in the cement and other industries has not been found. Similarly, very specific process information, that is not normally published, (e.g., information on operating schedules, waste treatment methods such as: evaporator pans, incinerators, etc.) would be required in order to properly estimate emissions for industries such as: wood preservation plants, some secondary metal producers and various other industrial processes that handle scrap materials (e.g., wire, drum or barrel incinerators, etc.). Hence, the values shown in Table 11.2.1 represent

only very approximate estimates. In relation to the total annual emissions estimates for Ontario, collective emissions from on-site industrial solid/liquid waste incineration facilities would appear to represent a significant potential contribution to PCDD and PCDF emissions relative to other sources. However, the number, locations and amounts of wastes burned in most Ontario industrial incinerators is not known. The other types of potential sources tabulated would appear to contribute relatively minor emissions of the toxic chemical classes of interest, in comparison with other emission sources. Furthermore, other probable emission sources of some of these chemicals, for which practically no data could be found include:

- pesticide manufacturers and formulators (e.g., data confidentiality),
- wastewater treatment plant aerobic systems,
- chemical spills and industrially-associated evaporative emissions,
- structural fires.

While data in the United States for many of the pesticides were not available for this study, it is possible to make an order of magnitude estimate for the entire U.S. for various years (1979 to 1986), based on preliminary pesticide useage estimates published by the U.S. EPA, Office of Pesticide Programs.

Table 11.2.2 provides these emission estimates. It is emphasized that the results in Table 11.2.2 should only be used to give some perspective to the other Eastern North America results and the proportions of the emission in this table which result from areas in the grid covered by the present study are not resolved. Based on the estimates in this table, none of the herbicides would rank higher than sixth, the insecticide indosulfan would rank third in its group.

Emissions of toxic materials from lakes and water courses are an ongoing subject of research and as yet no general methodology suitable for emissions estimates from these sources is available. While the broad

principles governing the emissions from, and depositions to, water bodies are reasonably well defined, applying these methods requires extensive and detailed data on air and water surface concentrations of the subject toxic. Such data are not available and while research estimates of the emissions/depositions have appeared in the literature for specific toxics, these results are as yet too sparse for the purposes of this inventory.

11.3 Data Limitations

Throughout the report, various notes and comments on the data quality have been made since air emissions data for many of the sources included in the inventory are limited. Similarly, the emission factors for various types of combustion sources which have been reported elsewhere or derived in this study, are based primarily on emission testwork that has often been directed toward a few of the strongest suspected contributing sources. In many instances, considerable variability exists in measuring trace or low levels of these semi-volatile organics in the emissions and both vapour and particle phases are not always determined. The test data are of prime importance since some of these pollutants are reported to form in the combustion process and could not feasibly be estimated by mass balance approaches. Thus, it must be emphasized that data are limited and highly variable for some sources and large potential uncertainties in the emission estimates can be expected. Furthermore, for some pollutants, this inventory provides an indication of the total emission magnitudes and source area locations, as well as an identification of the strong emission sources and specific data gaps for which future emphasis could be directed. Without other inventory comparisons it is presently difficult to determine the completeness or accuracy of these inventory data.

While the algorithms developed for estimations of the volatilization of applied pesticides provide a first estimate of the emissions for this inventory, more appropriate time-dependant numerical models are becoming available for simulating these emission processes. These more sophisticated models will require more detailed information on the time and mode of pesticide application. While the lack of such detailed data was not a limiting factor at the level of estimation achieved using the methods described in this report, future models will require such detail.

TABLE 11.2.1

Rough Estimate of Additional Emissions in Ontario for Potential Sources

Category/Sector	Estimated Potential Emissions (kg) PAH	PCB	PCDD	PCDF
Industrial				
Cement Production[1]	-	-	0.2	-
Asphalt Roofing Manufacture[2]	13	-	-	-
Wood Charcoal Production[2]	60	-	-	-
Wood Preservation - Creosote Plants[3]	30,000	-	0.003	0.002
- PCP Plants[3]	5,000	-	0.03	0.02
Incineration				
Industrial Sol./Liq. Waste Incin.[2]	2,000	0.3	4	3
Comm./Inst. Waste Incin. (Hosp.+ Apt.)[2]	200	0.2	0.08	0.2
Waste Oil Combustion[2]	-	0.9	-	-
Open Sources				
Res./Comm./Ind. On-site Burning[2]	600	-	-	-
Res./Comm./Ind. On-site Incin.[2]	500	0.4	0.1	0.1
Railway Tie Burning[4]	-	-	0.003	-
Pesticide (2,4-D) Application[5]	-	-	0.002	-
Total	38,000	1.8	4.4	3.3

Notes:

1. Based on emission tests at one Ontario plant with and without waste solvent fuel supplements (after deducting primary fuel contribution that has been assigned to the industrial fuel combustion sector).
2. Assuming potential Ontario sources contribute 5% of Eastern North American total emissions (i.e., base quantities lacking for Ontario).
3. Assumed evaporator pan emissions from one potential creosote plant and PCP plant in Ontario using reported PCDD and PCDF contents of these preservatives (Sheffield 1985).
4. Assumed 30% of used Canadian railway ties are burned in Ontario (Sheffield 1985) in conjunction with reported emission factors for burning preserved wood.
5. Based on the regulated maximum PCDD content of 2,4-D formulations (Sheffield 1985) and the estimated 2,4-D emission rate in Ontario in this study.

TABLE 11.2.2

Rough Estimates of Additional Pesticide Emissions for the Entire United States

Pesticide	Year	Emission kg/year
Butylate	1979	680,000
Linuron	1979	1,500,000
Metribuzin	1984	1,800,000
MCPA	1985	720,000
Endosulfan	1980	650,000
Lindane	1982	5,500
Methoxychlor	-	170,000
Captan	1982	3,400,000
Chloropicrin	1980	4,300,000
Dichloropropane	1982	16,000,000

12. CONCLUSIONS

In this preliminary but comprehensive inventory, annual speciated emissions of PAH, PCB, PCDD, PCDF and various pesticides to air during 1985 have been estimated and computed at the process level, using available data for point and area sources in Ontario and Eastern North America. The estimated emissions have also been geographically and temporally resolved to the UTM grid for Ontario and the modelling grid for other provinces and states in Eastern North America (ENA). Some of these estimates are regarded as first-cut data. The major conclusions from this inventory database are:

- total approximate emissions of the compound-specific classes in Ontario were estimated to be 272 tonnes of PAH, 50 kg PCB, 9.1 kg PCDD, 25 kg PCDF and 2,700 tonnes of various pesticides comprising specific herbicides, insecticides, fungicides and nematocides. Other potential sources, for which data are lacking, might contribute additional emissions in the order of 40 tonnes PAH, 2 kg PCB, 4 kg PCDD and 3 kg PCDF,

- sources in Ontario were estimated to contribute approximately 3% PAH, 5% PCB, 5% PCDD and 11% PCDF of the total annual ENA emissions of these compounds,

- emissions from a relatively few sectors (consisting of both point and area sources) were found to account for most of the emissions in each compound class and often the strongly-emitting sectors were common between the different pollutant classes. In Ontario, PAH emissions from residential wood combustion were found to clearly dominate other combustion sources; whereas, in ENA, major PAH sources included residential wood combustion, aluminum smelting, industrial and vehicular fuel combustion, as well as open burning and ferroalloy production. Transformer leakage was estimated to represent the strongest Ontario PCB source and the largest fraction of PCDD and PCDF emissions was determined to result from municipal waste incinerators, and secondary copper production, respectively. The latter source contribution is highly uncertain,

- the most volatile PAH species (e.g., acenaphthylene, methylphenanthrenes and phenanthrene) were emitted in the largest quantities of the defined PAH compounds and total emissions of benzo(a)pyrene were estimated to be approximately 2% of the 'total' PAH emissions. The relative proportions of some PAH compound emissions in Ontario generally compared favourable with the mean PAH profile of a series of ambient air measurements at a Toronto site. Similarly, the low to mid range chlorinated congeners of PCDD and PCDF were found to be the prevalent emissions. The species 2,3,7,8-TCDD was estimated to represent ~0.6% of the 'total' PCDD emissions (or approximately 57 g) during the year in Ontario, but it is recognized that this compound was not always measured in source emissions,
- the estimated 'total' PAH emissions derived for the gridded portion of the U.S. was compared with previous PAH inventory data for the entire U.S. Although such comparisons are only approximate, the relative importance of residential wood burning and some other sources was generally consistent between these inventories,
- as might be expected, the greatest emission densities of the combustion-related emissions (i.e., PAH, PCDD, PCDF) were located in areas of highest population in Ontario, due to contributions from sources such as residential wood and other fuel combustion and on-road vehicles. This is clearly evident from the greatest emission densities in the smallest UTM grid,
- in Ontario, of the pesticides studied, the largest emissions resulting from agricultural use are those of the soil fumigants dichloropropane and dichloropropene, which jointly represent 48% of the total emissions. In all, nematocides comprise 57% of the total emissions. The contributions to the emissions by those herbicides, insecticides and fungicides studied are estimated to be 39, 12 and 3%, respectively. The top ranking emissions of herbicides are due to alachlor and atrazine, while carbaryl and captan are the top ranking insecticide and fungicide emissions, respectively,
- within the Eastern North America domain, the emissions of the herbicides 2,4-D and alachlor are top ranking, while carbaryl and carbofuran lead the insecticide emissions. Fungicides and nematocide data were not available in the U.S.,
- with awareness of the several data limitations and uncertainties of the inventory, the compiled results can be expected to provide preliminary data input for modelling these emissions or further assessments of human exposure to these toxic chemicals.

13. RECOMMENDATIONS

Recommendations are provided here with intent to note improvements that can be made in any future emission compilations of these toxic chemicals. Specific recommendations pertaining to the air toxics and sources examined in this study follow:

- in order to focus efforts and achieve comparable emission inventories and/or emission factors, consideration should be given to defining a consistent and limited set of individual chemical compounds that are relevant to a given toxic chemical class (e.g., PAH compounds comprising a 'total'). This will also assist those measuring emissions, air quality or other environmental media and those using or interpreting data,

- information is needed, in order to improve emission estimates, regarding the practices, amounts and types of wastes incinerated at various types of industrial and commercial facilities in Ontario and Canada (e.g., on-site industrial incinerators, hospital and apartment incinerators, waste oil combustion and railway tie burning). For the compounds examined, the inventory status for some of these sources should be changed from area to point, so that more accurate assessments can be done,

- significant data gaps in published information apparently exist pertaining to both base quantity and emissions information for the wood preservation, pesticide manufacturing and ferrous foundry industries in Canada and elsewhere. Emission measurements at such facilities are recommended,

- because of the major estimated contributions of residential wood combustion emissions in Ontario, it is recommended to update previous wood consumption estimates, determine the extent and usage of wood stove emission controls that have been implemented in recent years, and re-define emission factors should recent emission test data be available to indicate reduced compound emissions due to controls,

- emission estimates of other specific major PAH sources should be improved with additional measurement data (e.g., vehicle age/deterioration impacts on gasoline and diesel vehicular

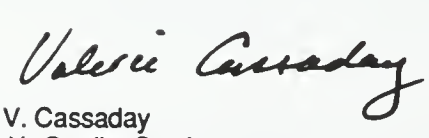
emissions, primary aluminum smelter measurements, ferroalloy and ferrous foundry data,

- a more in-depth examination of the secondary copper production sector would be required, in order to improve estimates of the PCDD and PCDF emissions for such sources,

- in order to make estimates of the pesticide emissions due to discontinued persistent pesticides such as DDT, dieldrin and others, comprehensive residue data on agricultural lands of resolution compared to pesticide use data should be gathered for modelling purposes,

- consideration should be given to applying a more sophisticated time-dependant numerical model for estimating annual pesticide emissions, as well as the seasonal and diurnal variations of their emissions,

- it is also recommended to plot and review data for all species for Ontario and U.S., since examination of such distributions may indicate those areas of the grid where data are lacking and those high emission areas where special attention should be given to refining the emission estimates in future studies.



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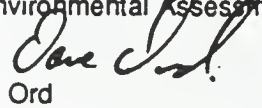

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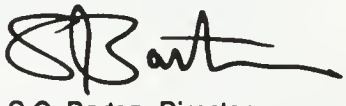

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REFERENCES

Accurex Corporation, 1986. "Dioxin Emissions from Industrial Boilers Burning Hazardous Materials". Prepared for U.S. Environmental Protection Agency. NTIS PB86-150620.

Alfheim, I. and Ramdahl, T., 1984. "Environmental Impact of Residential Wood Heating in Scandinavia". Presented at the 77th Annual Meeting of the Air Pollution Control Association, San Fransisco, California.

Alfheim, I. and Wikstrom, L., 1984. "Air Pollution from Aluminum Smelting Plants 1. The Emission of Polycyclic Aromatic Hydrocarbons and of Mutagens from an Aluminum Smelting Plant Using the Soderberg Process". Toxicological and Environmental Chemistry 8: 55-72.

Alliance Technologies, 1987. "Locating and Estimating Air Emissions from Sources of Polychlorinated Biphenyls (PCB)". Report to U.S. EPA, Office of Air Quality and Standards, EPA-450/4-84-007n.

Alsberg, T. and Stenberg, U., 1979. "Capillary GC and MS Analysis of PAH Emissions from Combustion of Peat and Wood in a Hot Water Boiler". Chemosphere 7: 487-496.

Alsberg, T., Stenberg, U., Westerholm, R., Strandell, M., Rannug, U., Sundvall, A., Romert, L., Bernson, V., Pettersson, B., Toftgard, R., Franzen, B., Jansson, M., Gustafsson, J.A., Egebäck, K and Tejie, G., 1985. "Chemical and Biological Characterization of Organic Material from Gasoline Exhaust Particles". Environ. Sci. Technol. 19(1):43-50.

Alter, H., 1977. "Man is Not the Only Polluter". Environmental Science and Technology 11(5): 442-448.

Amendola, G., Barna, D., Blosser, R., LaFleur, L., McBride, A., Thomas, F., Tiernan, T. and Whittemore, R., 1987. "The Occurrence and Fate of PCDDs and PCDFs in Five Bleached Kraft Pulp and Paper Mills". Presented at Seventh International Symposium on Chlorinated Dioxins and Related Compounds. Los Vegas, Nevada.

Barnes, H.M., 1985. "Trends in the Wood-Treating Industry: State-of-the-Art Report". Forest Products Journal 35 (1):13-22.

Bates, C.E. and Scheel, L.D., 1974. "Processing Emissions and Occupational Health in the Ferrous Foundry Industry". American Industrial Hygiene Association Journal 35(8):452-462.

Benestad C., Jebens, A. and Tveten, G., 1987. "Emission of Organic Micropollutants from Waste Incineration". Chemosphere 16(4):813-820.

Bennett, G.F., 1987. "Air Quality Aspects of Hazardous Waste Landfills". Hazardous Waste and Hazardous Materials. 4(2): 119-138.

Bergstrom, L.G.T. et al, 1981. "Chacterization and Comparison of Organic Emissions from Coal, Oil and Wood Fired Boilers". 6th International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle, Columbus, Ohio, October 27-28.

Beychok, M.R., 1987. "A Data Base of Dioxin and Furan Emissions from Municipal Refuse Incinerators". Atmos. Envir. 21(1): 29-36.

Bilsky, I.L., 1985. "Air Pollution Aspects of Hazardous Waste Disposal in Texas". Presented at the 78th Annual Meeting of the Air Pollution Control Association, Detroit, Michigan, June 16-21, 1985.

Bjorseth, A. and Ramdahl, T. (eds), 1985. "Handbook of Polycyclic Aromatic Hydrocarbons. Volume 2, Emission Sources and Recent Progress in Analytical Chemistry". Marcel Dekker Inc., New York.

Brooks, G., 1989. "Estimating Air Toxic Emissions from Coal and Oil Combustion Sources". Prepared by Radian Corporation for the U.S. Environmental Protection Agency. EPA - 450/2/-89-001. U.S. EPA, Research Triangle Park, North Carolina.

Brunner, C.R. and Brown, C.H., 1988. "Hospital Waste Disposal by Incineration". Journal of the Air Pollution Control Association 36(10):1297-1309.

Burlingame, J.E., Gabrielson, J.E., Langsjoen, P.L. and Cooke, W.M., 1981. "Field Tests of Industrial Coal Stoker-Fired Boilers for Inorganic Trace Element and Polynuclear Aromatic Hydrocarbon Emissions". Report prepared for the U.S. Environmental Protection Agency, U.S. Department of Energy and the American Boiler Manufacturers Association. EPA-600/7-81-167, PB82 230608, NTIS.

Carey, P., 1987. "Air Toxics Emissions from Motor Vehicles",. EPA-AA-TSS-PA-86-5. Office of Mobile Sources, U.S. Environmental Protection Agency.

Carhart, B.S. and Walsh, M.P., 1987. "Potential Contributions to Ambient Concentrations of Air Toxics by Mobile Sources". Paper 87-2.5. Presented at the 80th Annual Meeting of APCA, New York, New York, June 1987.

Chang, D.P.Y. and Hickman, D., 1989. "Biomedical Waste Incineration". Note to Editor, Journal of the Air Pollution Control Association 39(4):416.

Clement, R.E. Tosine, H.M. and Ali, B., 1985. "Levels of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Woodburning Stoves and Fireplaces". Chemosphere 14 (6/7): 815-819.

Committee on Pyrene and Selected Analogues, 1983. "Polycyclic Aromatic Hydrocarbons: Evaluation of Sources and Effects". Committee on Pyrene and Selected Analogues, Board on Toxicology and Environmental Health Hazards, Commission on Life Sciences, National Research Council. National Academy Press. As cited in U.S. EPA 1987.

Cooper, J.A., 1980. "Environmental Impact of Residential Wood Combustion Emissions and its Implications". Journal of the Air Pollution Control Association. 30(8): 855-867.

Crumpler, E.P., Rubin, A.B. and Bostian, H.E., 1988. "Status of U.S. EPA Sludge Incineration Regulations". Proc. Conf. on Municipal Sewage Treatment Plant Sludge Management, HMCRI, Silver Spring, Maryland.

Czuczwa, J.M. and R.A. Hites, 1986. "Airborne Dioxins and Dibenzofurans: Sources and Fates". Environmental Science and Technology 20(2): 195-200.

Dann, T., 1989. "Polycyclic Aromatic Hydrocarbons in the Ambient Air of Toronto, Ontario and Montreal, Quebec". Pollution Measurement Division, Environment Canada Report PMD 89-14, April.

DaRos, B., Merrill, R., Willard, H.K. and Wolbach, C.D., 1982. "Emission and Residue Values from Waste Disposal During Wood Preserving". Report prepared by Accurex Corp. for the U.S. Environmental Protection Agency. EPA-6002-82-062. U.S. EPA, Research Triangle Park, North Carolina.

Davies, J.A. and Allen, C.D., 1973. "Equilibrium, Potential and Actual Evaporation from Cropped Surfaces in Southern Ontario". J. of Ap. Met. 12: 649-657

DeAngelis, D.G. and Reznik, R.B., 1979. "Source Assessment: Residential Combustion of Coal". EPA-600/2-79-019a. U.S. Environmental Protection Agency, Research Triangle Park.

DeAngelis, D.G., et al, 1980. "Preliminary Characterization of Emissions from Wood-Fired Residential Combustion Equipment". EPA Report No. 600/7-80-040. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. As cited in U.S. EPA 1987a.

Des Rosiers, P.E. and Lee, A., 1986. "PCB Fires: Correlation of Chlorobenzene Isomer and PCB Homolog Contents of PCB Fluids with PCDD and PCDF Contents of Soot". Chemosphere 15 (8-12): 1313-1323.

Doskey, P.V. and A.W. Andren, 1981. "Modelling the Flux of Atmospheric Polychlorinated Biphenyls Across the Air/Water Interface". Environmental Science and Technology 15(6):705-711.

Doyle, B.W., Drum, D.A. and Lauber, J.D., 1985. "The Smoldering Question of Hospital Wastes". Pollution Engineering 17 (7):35-39.

Draper, W., 1986. "Quantitation of Nitro and Dinitropolycyclic Aromatic Hydrocarbons in Diesel Exhaust Particulate Matter". Chemosphere 15(4): 437-447.

Durkee, K.R., Noble, E.A. and Jenkins, R., 1977. "Standards Support and Environmental Impact Statement - Vol. 1.: Proposed Standards of Performances for Stationary Gas Turbines". EPA-450/2-77-017a. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. As cited in Shih et al 1979.

Eduljee, G., 1987. Volatility of TCDD and PCB from Soil". Chemosphere 16(4):907-920.

Edwards, C.A., 1975. "Persistent Pesticides in the Environment". 2nd Edition, CRC Press, Cleveland, Ohio.

Edwards, W.C. and Cotton, T., 1988. "VOC Emissions Methods Manual". Prepared by B.H. Levetton and Associates for Environment Canada.

Egebäck, K.E. (Ed.), 1982. "Chemical and Biological Characterization of Vehicle Exhaust Emissions, When Using Different Engine/Fuel Combinations". National Swedish Environment Protection Board, Stockholm. As cited in Stenberg et al 1983.

Ehrenfeld, J.R. and J.H. Ong., 1984. "Evaluation of Emission Controls for Hazardous Waste Treatment, Storage and Disposal Facilities". EPA-450/3-84-017. U.S. Environmental Protection Agency Research Triangle Park, North Carolina.

Eisenreich, S.J., B.B. Looney and J.D. Thornton, 1981. "Airborne Organic Contaminants in the Great Lakes Ecosystem". Environmental Science & Technology 15 (1):30-38.
Ekono Inc. 1976. "Environmental Pollution Control Pulp and Paper Industry. Part 1. Air." Report to U.S. Environmental Protection Agency. EPA-625/7-76-001.

Energy and Environmental Analysis Inc., 1978. "Preliminary Assessment of the Sources, Control and Population Exposure to Airborne Polycyclic Organic Matter (POM) as Indicated by Benzo(a)Pyrene". Draft submitted to the office of Air Quality, Planning and Standards, U.S. EPA.

Engineering-Science Inc., 1986. "Determination of Air Toxic Emissions from Non-Traditional Sources in the Puget Sound Region". U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Environment Canada, 1976. "Advances in Small-Scale Refuse Incinerators. Seminar Proceedings". Solid Waste Management Branch Report EPS-3-76-10.

Environment Canada, 1979. "Air Pollution Emissions and Control Technology: Wood Pulping Industry". Air Pollution Control Directorate Report EPS 3-AP-77-6.

Environment Canada, 1983a. "The Basic Technology of the Pulp and Paper Industry and its Environmental Protection Practices". Environmental Protection Programs Directorate Training Manual, EPS 6-EP-83-1.

Environment Canada, 1983b. "A Nationwide Inventory of Emissions of Air Contaminants (1978)". Report EPS 3-EP-83-10.

Environment Canada, 1983c. "Report on a Stack Sampling Program to Measure the Emissions of Selected Trace Organic Contaminants from the Hamilton/Wentworth Sewage Sludge Incinerator". Environmental Protection Programs Directorate, October.

Environment Canada, 1983d. "Report on the Stack Sampling Program to Measure the Emission of Selected Trace Organic Compounds, Particulates, Heavy Metals and HCl from the Royal Jubilee Hospital Incinerator, Victoria, British Columbia". Environmental Protection Programs Directorate, April.

Environment Canada, 1985. "Report on the Characterization of Particulate and Gaseous Emissions from the Coal-Fired Coal Dryer at Bullmoose Operating Corporation, Tumbler Ridge, British Columbia". Environmental Protection Programs Directorate.

Environment Canada, 1986a. "Agricultural Pesticide Retail Inventory, Prince Edward Island". Conservation and Protection, Atlantic Region, EP-5-AR-88-2.

Environment Canada, 1986b. "Emissions and Trends of Common Air Contaminants in Canada: 1970-1980". Program Management Branch Report EPS 7/AP/17, September.

Environment Canada, 1988. "Agricultural Pesticide Retail Inventory, Nova Scotia". Conservation and Protection, Atlantic Region, EP-5-AR-88-1, 1988.

Environment Canada, 1988b. "Inventory of Polycyclic Aromatic Hydrocarbons Sources in Quebec - Abridged Version". Reported prepared by Lavalin Environment for Conservation and Protection, Environment Canada.

Environment Protection Service (EPS), 1985a. "Fires in Electrical Equipment Containing PCBs: Recommendations to Prevent Contamination by PCDFs". Report EPS 1/CC/2 prepared by the Commercial Chemicals Branch, Environment Canada, March.

Environment Protection Service (EPS), 1985b. "Report on the Emission Testing for Dioxins, Furans and Chlorophenols from the Combustion of Preserved Railroad Ties in a Domestic Furnace". Environment Canada Unpublished Report.

Environmental Application Group, 1984. "1980 Ontario VOC Emissions Inventory". Report prepared for the Ontario Ministry of the Environment, November.

Erickson, M.D. et al, 1985. "PCDF Formation from PCBs under Fire Conditions". Chemosphere 14 (6-7): 855-858.

Evans, J.C., Abel, K.H., Olsen, K.B., Lapel, E.A., Sanders, R.W., Wilkerson, C.L., Hayes D.J., Mangelson, N.F. and Perkins, R.W., 1985. "Characterization of Trace Constituents at Canadian Coal-Fired Power Plants. Vol. 1. Phase I Final Report". Prepared by Battelle Pacific Northwest Laboratories for the Canadian Electrical Association.

Fellin, P., Davis, C.S. and Fradkin, R., 1985. "A Critical Review of Nitro-and Oxy-PAH Compounds in the Environment". Prepared by Concord Scientific Corporation for Atmospheric Environment Service.

Fiat, 1980. "Emissions of PAH Reactive and Non-Reactive Hydrocarbons and Aldehydes from Current Production Cars". Accordo di Ricerca Feemas. As cited in Stenberg et al 1983.

Fisheries and Environment Canada, 1977. "Literature Review of Wastewater Characteristics and Abatement Technology in the Wood and Timber Processing Industry". Economic and Technical Review Report, EPS 3-WP-77-2, Environmental Protection Service.

Fisheries and Environment Canada, 1978. "The Timber Processing Industry - Seminar Proceedings". Economic and Technical Review Report EPS-3-WP-78-1. Environmental Protection Service.

Fitzgerald, E.F., Standfast, S.J., Youngblood, L.G., Melius, J.M. and Janerich, D.T., 1986. "Assessing the Health Effects of Potential Exposure to PCBs, Dioxins and Furans from Electrical Transformer Fires: The Binghamton State Office Building Medical Surveillance Program". Archives of Environmental Health 41 (6):368-376.

Frank, R and Braun, H.E., 1981. "Residues from Past Uses of Organochlorine Insecticides and PCB in Waters Draining Eleven Agricultural Watersheds in Southern Ontario, Canada, 1975-1977". The Science of the Total Environment 20:225-276.

Friesen, K.J., Sarna, L.P. and R.B. Webster, 1985. "Aqueous Solubility of Polychlorinated Dibenzo-p-dioxins Determined by High Pressure Liquid Chromatography", Chemosphere 14 (9): 1267-1274.

Fuchs, M.R., et al, 1984. "Emission Test Report: T.J. Campbell, Asphalt Concrete Plant, Oklahoma City, Oklahoma". EPA/EMB Report No. 83-ASP-4. Office of Air Quality Planning and Standards, U.S. EPA, Research Triangle Park, North Carolina as cited in U.S. EPA 1987a.

Furr, A.K., Lawrence, A.L., Tong, S.C., Grandolfo, M.C., Hofstader, R.A., Bache, C.A., Gutenmann, W.H. and Lisk, D.J., 1976. "Multielemental and Chlorinated Hydrocarbon Analysis of Municipal Sewage Sludges of American Cities". Environmental Science and Technology 10(7): 683-687.

Gerstle, R.W., Kemner, W.F. and Yerino, L.V., 1980. "Review of Performance Standards for Ferroalloy Production Facilities". EPA-450/3-80-41. Prepared by PEDCO Environmental Inc., for U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Giammar, R.D., Engdahl, R.B. and Barrett, R.E., 1976. "Emissions from Residential and Small Commercial Stoker-Fired Boilers Under Smokeless Operation". EPA-600/7-76-029, U.S. Environmental Protection Agency, Research Triangle Park.

Gianessi, L.P., and C.A. Puffer, 1988. "Use of Selected Pesticides in Agricultural Crop Production by State - Use Coefficients by State". Resources for the Future, Quality of the Environment Division.

Gibson, T.L., 1982. "Nitroderivatives of Polynuclear Aromatic Hydrocarbons in Airborne and Source Particulate". Atmos. Environ. 16:2037-2040. As cited in U.S. EPA 1987a.

Grant, W.J., 1985. "Canadian Petroleum Refineries Atmospheric Emission Survey, 1983". PACE Report 85-1. Prepared for the Petroleum Association for Conservation of the Canadian Environment (PACE).

Great Lakes Science Advisory Board, 1981. "1981 Annual Report by the Committee on the Assessment of Human Health Effects of Great Lakes Water Quality".

Greenfield, M. (Dofasco), 1989. Personal Communication. July.

Gross, G.P., 1970. "First Annual Report on Gasoline Composition and Vehicle Exhaust Gas Polynuclear Aromatic Content". U.S. Department of Health, Education and Welfare, Durham, North Carolina. As cited in U.S. EPA 1987a.

Gross, G.P., 1982. "Gasoline Composition and Vehicle Gas Polynuclear Aromatic Content". CRC-APRAC Project. CAPE-6-68. As cited in Stenberg et al 1983.

Gwin, C.H., W.D. Scott and James, R.B., 1976. "A Preliminary Investigation of the Organic Chemical Emissions from Green Sand Pyrolysis". American Industrial Hygiene Association Journal 37(12):685-689.

Haile, C., Stanley, J.S., Walker, T., Cobb, G.R. and Boomer, B.A., 1983. "Comprehensive Assessment of the Specific Compounds Present in Combustion Processes. Volume 3. National Survey of Organic Emissions from Coal-fired Utility Boiler Plants". EPA-560-/5-83-006, Office of Toxic Substances.

Hall, R.E. and D.G. DeAngelis, 1980. "EPA's Research Program for Controlling Residential Wood Combustion Emissions". Journal of the Air Pollution Control Association 30 (8): 862-867. August 1980. As cited in U.S. EPA 1987a.

Hallett, D., 1985. "Dioxin in the Great Lakes Ecosystem: A Canadian Perspective". Chemosphere 14(6-7):745-753.

Handa, T., Yamamura, T., Kato, Y., Sarto, S. and Ishii, T., 1979. "The Effect of Automotive Operating Conditions on Polynuclear Aromatic Hydrocarbon Emissions". J. Japan Soc. Air Pollut. 14:334-339. As cited in Stenberg et al 1983.

Hangebrauck, R.P., Lauch, R.P. and Meeker, J.E., 1966. "Emissions of Polynuclear Hydrocarbons from Automobiles and Trucks". Am. Ind. Hyg. Assoc. J. 1:47-56. As cited in Stenberg et al 1983.

Hangebrauck, R.P., von Lehmden, P.J. and Meeker, J.E., 1967. "Sources of Polynuclear Hydrocarbons in the Atmosphere". Public Health Service Report No. AP-33. U.S. Department of Health and Welfare, Public Health Service, Cincinatti.

Hartman, M.W. and Rives, G.D., 1985. "Literature Review and Survey of Emissions from Residential Wood Combustion and their Impact". EPA Report No. 660/2-85-047. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. As cited in U.S. EPA 1987a.

Hay, D.J., Finkelstein A. and Klicius, R., 1986. "The National Incinerator Testing and Evaluation Program Two Stage Incinerator Combustion Test". Chemosphere 15 (9-12): 1201-1212.

Hoekman, S.K. and Ingham, M.C., 1987. "Measurement of PAH and Nitro-PAH from a Heavy-Duty Diesel Engine". Paper No. 87-1.4. Presented at the 80th Annual Meeting of APCA, New York, New York, June 1987.

Hoff, R.M. and K. Chan, 1987. "Measurement of Polycyclic Aromatic Hydrocarbons in the Air along the Niagara River". Environmental Science and Technology 21 (6):556-561.

Houle, G., "Emissions des Hydrocarbures Polycyclic Aromatiques Provenant de L'Aluminerce de la Compagnie Secal a Jonquiere". Ministere de L'Environment, Direction de L'Assainissement de L'Air, Decembre 1986.

Hunt, G.T., Wolf P., and Fennelly, P.F., 1984. "Incineration of Polychlorinated Biphenyls in High Efficiency Boilers: A Viable Disposal Option". Environmental Science and Technology, 18 (3): 171-179.

Hurley, J.F. and Hersh, S., 1977. "Effect of Smoke and Corrosion Suppressant Additives on Particulate and Gaseous Emissions from a Utility Gas Turbine". Prepared by KVB Inc., for Electric Power Research Institute. EPRI FP-398.

Knight, C.V. et al, 1983. "Polynuclear Aromatic Hydrocarbons and Associated Organic Emissions from Catalytic and Noncatalytic Wood Heaters". In: Polynuclear Aromatic Hydrocarbons: Formation, Mechanism and Measurement, Proceedings of the Seventh International Symposium on Polynuclear Aromatic Hydrocarbons, 1982, Columbus, Ohio. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. As cited in U.S. EPA 1987a.

Kraft, J. and Lees, K.H., 1981. "Polycyclic Aromatic Hydrocarbons in the Exhausts of Gasoline and Diesel Vehicles". SAE Paper No. 810082. Society of Automotive Engineers, Warrendale, PA. As cited in Stenberg et al 1983.

Lahre, T.F., 1986. "Compiling Air Toxics Emission Inventories", U.S. Environmental Protection Agency, EPA-450/4-86, July.

Lang, J.M., Snow, L., Carlson, R., Black, F., Zweidinger, R. and Tejada, S., 1981. "Characterization of Particulate Emissions from In-Use Gasoline-Fueled Motor Vehicles". SAE Paper 811186. Society of Automotive Engineers, Warrendale, PA. As cited in U.S. EPA 1987a.

Lao, R.C., et al, 1983. "Investigation of PAH and Polychlorinated Organic Pollutant Emissions from Wood Combustion Sources". In: Polynuclear Aromatic Hydrocarbons: Formation, Mechanism, and Measurement, Proceedings of the Seventh International Symposium on Polynuclear Aromatic Hydrocarbons, 1982, Columbus, Ohio. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. As cited in U.S. EPA 1987a.

Larsen, S., 1984. "Automotive Emission Factors: An Indirect Measurement Applied to Polycyclic Aromatic Hydrocarbon and Lead Emissions". Paper No. 84-72.4, presented at the 77th Annual Meeting of the Air Pollution Control Association, San Francisco, Calif., June 24-28.

Larsson, P., 1985. "Contaminated Sediments of Lakes and Oceans Act as Sources of Chlorinated Hydrocarbons for Release to Water and Atmosphere". Nature 317: 347-349.

Leistra, M., 1973. "Computation Models for the Transport of Pesticides in Soil". Residue Reviews 49: 87-130.

Lewis, R.G. and E. Lee, Jr., 1976. "Air Pollution from Pesticides and Agricultural Processes: Sources, Occurrence and Dispersion", Report prepared by US Environmental Protection Agency, Published by CRC Press, Cleveland, Ohio.

Lewis, R.G., B.E. Marlin, 1985. "Measurement of Fugitive Atmospheric Emissions of Polychlorinated Biphenyls from Hazardous Waste Landfills". Environmental Science and Technology 19 (10): 986-991.

Lewis, R.G., et al, 1986. "Monitoring for Non-Occupational Exposure to Pesticides in Indoor and Personal Respiratory Air". Paper No. 86-37-4 presented at the 79th Annual Meeting of the Air Pollution Control Association, Minneapolis, Minn., June 22-27.

Longley, W.R., 1989. "An Air Toxics Emission Inventory of a Select Group of Polycyclic Aromatic Hydrocarbons (PAHs) for the City of Mississauga". Master's Thesis, Erindale Campus, University of Toronto.

Mackay, D. and S. Paterson, 1982. "Fugacity Revisited". Environmental Science and Technology 16(12): 654A-660A.

Marklund, S., Rappe, C. and Tysklind, M., 1987. "Identification of Polychlorinated Dibenzofurans and Dioxins in Exhausts from Cars Run on Leaded Gasoline". Chemosphere 16(1):29-36.

Masclet, P., Bresson, M.A. and Mouvier, G., 1987. "Polycyclic Aromatic Hydrocarbons Emitted by Power Stations and Influence of Combustion Conditions". Fuel 66: 556-562.

Masclet, P., Mouvier G. and Nikolaou, K., 1986. "Relative Decay Index and Sources of Polycylcic Aromatic Hydrocarbons". Atmospheric Environment 20(3):439-446.

McCarley, W.R., Moskowitz, C.M., Ochner, J.C. and Reznik, R.B., 1979. "Source Assessment: Dry Bottom Industrial Boilers Firing Pulverized Bituminous Coal". Prepared by Monsanto Research Corp. for the U.S. Environmental Protection Agency, EPA-600/2-78-004.

McGee, B., 1984. "Survey of Pesticide Use in Ontario, 1983. Estimates of Pesticides Used on Field Crops, Fruits, Vegetables and in Roadside Weed Control". Economics Information Report No. 84-05, Economics and Policy Coordination Branch, Ontario Ministry of Agriculture and Food.

McInnes, R.G. and Hunt, G.T., 1986. "Critical Criteria in the Development of a Toxic Air Emissions Inventory for Municipal Solid Waste Incinerators". Paper presented at the Spring 1986 Conference "Environmental Implications of Resource Recovery", Providence, RI, April 22-23.

McIntyre, A.E. and Lester, J.N., 1984. "Occurrence and Distribution of Persistent Organochlorine Compounds in UK Sewage Sludges". Water, Air and Soil Pollution 23:397-415.

McKee et al, 1978. "Unregulated Emissions from a PROCO Engine-Powered Vehicle", Society of Automotive Engineers Paper No. 780592, Warrendale, PA. As cited in Carhart and Walsh 1987.

McKellar, K., 1988. Personal Communication. June.

Micklewright, J.T., 1988. "Wood Preserving Plants in the United States, 1986". Prepared for the American Wood Preservers Institute, Vienna, Virginia.

Miller, C.O.M., 1980. "A Mathematical Model of Aerial Deposition of Pesticides from Aircraft". Environmental Science and Technology, 14(7):824-831.

Miller, S.E. and Barrett, R.E., 1975. "Sampling and Analysis of Source Emission Samples from a Carbon Black Plant". EPA/EMB Report No. 75-CBK-2. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Ministry of the Environment (MOE), 1979. "Polynuclear Aromatic Hydrocarbons A Background Report Including Available Ontario Data". Ontario Ministry of the Environment ARD-TDA-Report No. 58-79. September.

Ministry of the Environment (MOE), 1984b. "Determination of Chlorinated Dibenzo-p-Dioxins, Chlorinated Dibenzofurans, Chlorinated Biphenyls, Chlorobenzenes and Chlorophenols in Air Emissions and Other Process Streams at SWARU in Hamilton". MOE Report No. ARB-02-84-ETRD.

Ministry of the Environment (MOE), 1985. "Scientific Criteria Document for Standard Development No. 4-84-Polychlorinated Dibenzo-p-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs)". September.

Ministry of the Environment (MOE), 1986. "Incinerator Design and Operating Criteria - Volume II - Biomedical Waste Incinerators". October.

Mogan, J.P., Westaway, K.C., Horten, A.J. and Dainty, E.D., 1983. "Polynuclear Aromatic Hydrocarbons and Mutagens in the Air of Underground Dieselized Mines". Presented at the 10th World Congress on the Prevention of Occupational Accidents and Diseases, May 9, 1983, Ottawa, Canada.

Morales, J.A., Escalona, L., Ishizaki C. and Sanhueza, E., 1979. "Forest Fires: An Important Source of Benzo(a)pyrene in the Caracus Valley". Journal of the Air Pollution Control Association 29(10):1072-1073.

Mumma, R.O., Ranpach, D.R., Waldman, J.P., Hotchkiss, J.H., Gutenmann, W.H., Bache, C.A. and Lisk, D.J., 1983. "Analytical Survey of Elements and Other Constituents in Central New York State Sewage Sludges". Arch. Environ. Contam. Toxicol. 12:581-587.

Murphy, T.J. and C.P. Rzeszutko, 1977. "Precipitation Inputs of PCBs to Lake Michigan". International Association Great Lakes Research 3(3-4): 305-312.

Murphy, T.J., Formanski, L.J., Brownawell, B. and Meyer, J.A., 1982. "PCB Emissions to the Atmosphere from Municipal Landfills and Incinerators". Reprinted Extended Abstract of Paper Presented at the American Chemical Society, Kansas City, Mo., September.

Murphy, T.J., Formanski, L.J., Brownawell, B. and Meyer, J.A., 1985. "Polychlorinated Biphenyl Emissions to the Atmosphere in the Great Lakes Region. Municipal Landfills and Incinerators". Environmental Science and Technology 19(10): 942-946.

Murphy, T.J., M.D. Mullin and J.A. Meyer, 1987. "Equilibration of Polychlorinated Biphenyls and Toxaphene with Air and Water". Environmental Science and Technology 21(2):155-162.

National Air Toxics Information Clearing House (NATICH), 1988. "NATICH Data Base-Source Reports". As of April 1988.

National Research Council of Canada (NRCC), 1983. "Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Formation, Sources, Fate and Effects in Aquatic Biota". NRC Associate Committee on Scientific Criteria for Environmental Quality Publication No. NRCC 18981.

Nestrick, T.J. and Lamparski, L.L., 1982. "Isomer-Specific Determination of Chlorinated Dioxins for Assessment of Formation and Potential Environmental Emission from Wood Combustion". Anal. Chem. 54:2292-2299.

Nishioka, M., Chang, H. and Lee, M.L., 1986. "Structural Characteristics of Polycyclic Aromatic Hydrocarbon Isomers in Coal Tars and Combustion Products". Environ. Sci. Technol. 20(10): 1023-1027.

Oehme, M., Mano, S. and Mikalsen, A., 1987. "Formation and Presence of Polyhalogenated and Polycyclic Compounds in the Emissions of Small and Large Scale Municipal Waste Incinerators". Chemosphere 16(1):143-153.

Ontario Ministry of Agriculture and Food, 1988a. "1988 Field Crop Recommendations", Publication 296.

Ontario Ministry of Agriculture and Food, 1988b. "Fruit Production Recommendations", Publication 360.

Ontario Ministry of Agriculture and Food, 1988c. "Production Recommendations for Ornamentals and Turf", Publication 383.

Ontario Ministry of Agriculture and Food, 1989a. "Guide to Weed Control; 1989". Publication 75.

Ontario Ministry of Agriculture and Food, 1989b. "1989 Vegetable Production Recommendations", Publication 363 supp.

Ontario Ministry of Natural Resources (MNR), 1986. "Statistics 1986-A Statistical Supplement to the Annual Report of the Minister of National Resources for the Year Ending March 31, 1986".

Ontario Research Foundation (now ORTECH International), 1983. "Area Source Emission Inventory of Nitrogen Oxides in Ontario. Final Report". Prepared for the Ontario Ministry of the Environment.

Ontario Research Foundation (now ORTECH International), 1985. "A Preliminary Assessment of Wood Burning Emissions in Ontario". ORF Report P-4254/G. Prepared for the Ministry of Energy, Province of Ontario.

Oppelt, E.T., 1987. "Incineration of Hazardous Waste. A Critical Review". J. Air Pollution Control Assoc. 37 (5): 558-585.

Orris, P., Kominsky, J.R., Hryhorczuk, D. and Melius, J., 1986. "Exposure to Polychlorinated Biphenyls from an Overheated Transformer". Chemosphere 15(9-12):1305-1311.

ORTECH International, 1989. "Mutagenicity and Chemical Composition of Coke Oven Emissions". G.H. Thomas and A.J. Horton, ORTECH International Report No. P.88-46-5019-OG-03, prepared for the Ontario Ministry of the Environment. June.

Ozvacic, V., Wong, G.,Tosine, G., Clement, R.E. and Osborne, J., 1985. "Emissions of Chlorinated Organics from Two Municipal Incinerators in Ontario". Journal of the Air Pollution Control Association 35(8):849-855.

Palmer, W.G. and Scott, W.D., 1981. "Lung Cancer in Ferrous Foundry Workers: A Review". American Industrial Hygiene Associaton Journal 42(5):329-340.

Parsons, T. (Ed.), 1977. "Industrial Process Profiles for Environmental Use: Chapter 24. The Iron and Steel Industry". Radian Corp. Report. EPA-600/2-77-023x. February.

PEI Associates Inc., 1985. "Organics Screening Study Test Report - Sewage Sludge Incinerator No. 13, Detroit Water and Sewer Department, Detroit, Michigan". Report to U.S. Environmental Protection Agency, Report No. EMB 85-CHM-5, June.

Peters, J.A., 1982. "POM Emissions from Residential Woodburning: An Environmental Assessment". In: Proceedings of the 1981 International Conference on Residential Solid Fuels - Environmental Impacts and Solutions. Portland, Oregon. June 1-4, 1981. J.A. Cooper and D. Malek, eds. Oregon Graduate Center, Beaverton, Oregon, 1982. As cited by U.S. EPA 1987a.

Peters, J.A., et al, 1981. "An Environmental Assessment of POM Emissions from Residential Wood-fired Stoves and Fireplaces". In: Polynuclear Aromatic Hydrocarbons: Chemical Analysis and Biological Fate, Proceedings of the Fifth International Symposium on Polynuclear Aromatic Hydrocarbons, 1980, Columbus, Ohio. M. Cooke and A. Dennis, eds. Battelle Press, Columbus, Ohio. As cited in U.S. EPA 1987a.

Piersol, P., 1989. "The Evaluation of Mobile and Stationary Facilities for the Destruction of PCBs". ORTECH International, Envirochem Services and Monenco Ltd. Report to Environment Canada, Report EPS 3/HA/5, May.

Powell, F.C., 1987. "Air Pollutant Emissions from the Incineration of Hospital Wastes, The Alberta Experience". Hazardous Waste Management 37 (7):836-839.

Priestly, C.H.D. and Taylor, R.J., 1972. "On the Assessment of Surface Heat Flux and Evaporation Using Large Scale Parameters". Mon. Wea. Rev. 100: 81-92.

Radian Corporation, 1987. "Hospital Waste Combustion Study Data Gathering Phase Final Draft Report". Prepared for Pollutant Assessment Branch, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, October.

Ramdahl, T., Alfheim, I. and Bjoerseth, A., 1981. "Sources and Emission Factors of Polycyclic Aromatic Hydrocarbons". NTIS PB.83-132464.

Ramdahl, T., Alfheim, I., Rustad, S. and Olsen, T., 1982. "Chemical and Biological Characterization of Emissions from Small Residential Stoves Burning Wood and Charcoal". Chemosphere 11(6): 601-611.

Reiss, R. and J. Pare, 1984. "Les pesticides en agriculture au Quebec en 1982", Environmental Canada, Environmental Protection Service, Quebec Region.

Ritcey, G., F.L. McEwen, H. Braun and R. Frank, 1981. "Initial Pesticide Residues in Relation to Vapour Pressure". Pesticide Science 12:614-618.

Robertson, D.J., Groth, R.H. and Blasko, T.J., 1980. "Organic Content of Particulate Matter in Turbine Engine Exhaust". JAPCA 30 (3):261-266.

Rordorf, B.F., 1989. "Prediction of Vapour Pressure, Boiling Points and Enthalpies of Fusion for Twenty-nine Halogenated Dibenzo-p-dioxins and Fifty-five Dibenzofurans by a Vapor Pressure Correlation Method". Chemosphere 18 (1-6): 783-788.

Rudolph, J.L., Harris, J.C., Grosser, Z.A. and Levins, P.L., "Ferroalloy Process Emissions Measurements". EPA-600/2-79-045. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Sanborn, C.R., Cooke, M., Bresler, W. and Osborne, M.C. 1985. "Characterization of Emissions of PAHs from Residential Coal-Fired Space Heaters". EPA/600/D-85/243. U.S. Environmental Protection Agency, Research Triangle Park.

Schimberg, R.W., Pfaffli P. and Tossavainen, A., 1980. "Polycyclic Aromatic Hydrocarbons in Foundries", Journal of Toxicology and Environmental Health 6:1187-1194.

Schuetzle, D. and Perez, J.M., 1983. "Factors Influencing the Emissions of Nitrated-Polynuclear Aromatic Hydrocarbons (Nitro-PAH) from Diesel Engines". Journal of the Air Pollution Control Association. 33(8): 751-755.

Science Applications International Corp., 1987. "Data Base on Incineration of Municipal Sludge". Draft Report to U.S. Environmental Protection Agency, Contract No. 68-01-6941, June 15.

Scott, W.D., James R.H. and Bates, C.E., 1976. "Foundry Air Contaminants from Green Sand Molds", American Industrial Hygiene Association Journal June: 335-344.

Seiber, J.N. and J.E. Woodrow, 1983. "Methods for Studying Pesticide Atmospheric Dispersal and Fate at Treated Areas". Residue Reviews, 85:217-229.

Seibert, P.C., Alston, D.R., Walsh J.F. and Jones, K.H., 1987. "Statistical Properties of Available Worldwide MSW Combustion Dioxin/Furan Emissions". APCA Paper 87-94.1 presented at the 80th Annual APCA Meeting, New York, NY, June 21-26.

Sep, M., 1989. Personal Communication, Pratt and Whitney Corporation, March. As reported by Longley (1989).

Serth, R.W. and Hughes, T.W., 1980. "Polycyclic Organic Matter (POM) and Trace Element Contents of Carbon Black Vent Gas". Environ. Sci. Technol. 14(3): 298-301.

Shanks, G., 1985. "Pesticide Usage in New Brunswick". Province of New Brunswick, Environmental Services Branch, Municipal Affairs and Environment.

Sheffield, A., 1985. "Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs): Sources and Releases". Environmental Protection Service, Environment Canada, Report EPS 5/HA/2, July.

Sheidl, K., Wurst, F. and Kuna, R.P., 1986. "Dioxin and Furan Emissions from a Fluidized-Bed Incinerator During the Combustion of Paper Recycling Residues". Chemosphere 15 (9-12): 2089-2092.

Shen, T., 1981. "Estimating Hazardous Air Emission from Disposal Sites". Pollution Engineering, August: 31-34.

Shen, T.T., and T.J. Tofflemire, 1980. "Air Pollution Aspects of Land Disposal of Toxic Wastes". Journal of the Environmental Engineering Division, February: 221-226.

Shih, C.C., Hamersma, J.W., Ackerman, D.G., Beimer, R.G., Kraft, M.L. and Yamada, M.M. 1979. "Emissions Assessment of Conventional Stationary Combustion Systems; Volume II. Internal Combustion Sources". Prepared for the U.S. Environmental Protection Agency, EPA/600-13, PB-296 390.

Shih, C.C., Orsini, R.A., Ackerman, D.G., Moreno, R., Moon, E.L., Scinto, L.L. and Yu, C., 1980. "Emissions Assessment of Conventional Stationary Combustion Systems: Volume III. External Combustion Sources for Electricity Generation". EPA-600/7-81-003a.

Shoakat, R.K. and M.C. Spearin, 1985. "Data sources related to pesticide use in Canadian Agriculture". Working paper prepared for Agriculture Canada, Regional Development Branch, Development Policy Directorate.

Siebert, P.C., 1978. "Preliminary Assessment of the Sources, Control and Population Exposure to Airborne Polycyclic Organic Matter (POM) as Indicated by Benzo(a)pyrene (BaP)". Prepared under EPA Contract No. 68-02-2836. Pollutant Strategies Branch, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

Siedhoff, T.E., 1985. "An Alternative Method for High Level PCB Destruction". Paper 85-68.4 presented at the 78th Annual Meeting of the Air Pollution Control Association, Detroit, Michigan, June 16-21.

Smith, I.M., 1984. "PAH from Coal Utilization - Emissions and Effects". No. PB-85-17728-5, IEA Coal Research, London.

Spicer, C.W., Holdren, M.W., Miller, S.E., Smith, D.L., Smith, R.N. and Hughes, D.P., 1988. "Aircraft Emissions Characterization". Prepared by Battelle Columbus Division for Engineering and Services Laboratory. ESL-TR-87-63.

Staiff, D.C., Quinby, G.E., Spencer, D.L. and Starr, H.G. Jr., 1974. "Polychlorinated Biphenyl Emissions from Fluorescent Lamp Ballasts". Bulletin of Environmental Contamination and Toxicology 12(4):455-463.

Standley, L.J. and Simoneit, B.R.T., 1987. "Characterization of Extractable Plant Wax, Resin, and Thermally Matured Components in Smoke Particles from Prescribed Burns". Environmental Science and Technology 21(2):163-169.

Stenberg, U., 1979. "The Emisson of Polynuclear Aromatic Hydrocarbons from Gasoline-Powered Vehicles". Report to the Swedish EPA, February. As cited in Stenberg et al, 1983.

Stenberg, U., Alsberg, T. and Westerholm, R., 1983. "Emission of Carcinogenic Components with Automobile Exhausts". Environmental Health Perspectives. 47: 53-63.

Suntio, L.R., Shin, W.Y., MacKay, D., Seiber, J.N. and Glotfelty, D., 1988. "Critical Review of Henry's Law Constants for Pesticides". Rev. of Environ. Contaminants and Toxicology 103.

Surprenant, N.F., Battye, W., Roeck, D. and Sandberg, S.M., 1981. "Emissions Assessment of Conventional Stationary Combustion Systems: Vol. V. Industrial Combustion Sources." Prepared for the U.S. Environmental Protection Agency, EPA-600/7-81-003c, PB 81-225559.

Surprenant, N.F., Hung, P., Li, R., McGregor, K.T., Piispanen, W. and Sandberg, W.S., 1981a. "Emissions Assessment of Conventional Statonary Combustion Systems: Volume IV, Commercial/Institutional Combustion Sources". Report prepared for the U.S. Environmental Protection Agency. EPA-600/7-81-003b, PB 81 145 187, NTIS.

Swanson, S.E., Rappe, C., Malström, J. and Kringstad, K.P., 1988. "Emissions of PCDDs and PCDFs from the Pulp Industry". Chemosphere 17(4):681-691.

Taylor, A.W., 1978. "Post-Application Volatilization of Pesticides under Field Conditions". Journal of the Air Pollution Control Association 28(9):922-927.

Tejada, S.B., Zweidinger, R.B. and Sigsby, J.E., 1982. "Analysis of Nitroaromatics in Diesel and Gasoline Car Emissions". SAE Paper 820775. Society of Automotive Engineers, Warrendale, PA.

Thorndyke, S.J., 1980. "Stack Testing at the Woodward Avenue Sewage Treatment Plant Sludge Incinerator". Ontario Research Foundation Report P-2794 to Ontario Ministry of the Environment (West Central Region), July 23.

Thorndyke, S.J., 1984. "Environmental Testing During Liquid Industrial Waste Burning in a Rotary Cement Kiln for Canada Cement Lafarge Limited Plant No. 4 Woodstock, Ontario". Ontario Research Foundation Report P-4391/I.

Thorndyke, S.J., 1986. "Environmental and Chemical Engineering Division, Ontario Research Foundation, "ARB Trace Organic Contaminants Sampling at Municipal Incinerators". ORF Report 46-41008 for the Ontario Ministry of the Environment.

White, L.D., Stasikowski, M.J., Horstman, S.W. and Bingham, E., 1975. "Atmospheric Emissions of Coking Operations - A Review". Report prepared by the Department of Health, University of Cincinnati Medical Centre, Cincinnati, Ohio.

Williams, R.L. and Swarin, S.J., 1981. "Benzo(a)pyrene Emissions from Gasoline and Diesel Automobiles". Society of Automotive Engineers, Warrendale, PA. Paper No. 790419. As cited in Stenberg et al 1983.

Willis, G.H. and L.L. McDowell, 1987. "Pesticide persistence on Foliage". Review of Environmental Contamination and Toxicology, 100.

Willis, G.H., L.L. McDowell, L.M. Southwick and S. Smith, 1985. "Toxaphene, Methyl Parathion and Fenvalerate Disappearence from Cotton Foliage in the Mid-South". Journal of Environmental Quality 14(3):446-450.

Willis, G.H., L.L. McDowell, S. Smith and L.M. Southwick, 1986. "Permethrin Washoff from Cotton Plants by Simulated Rainfall". Journal of Environmental Quality 15(2):116-120.

York Research Corporation, 1979. "Coke Quench Tower Emission Testing Program". EPA-600/2-79-082. April.

Young, T.M. and Ostermeier, D.M., 1987. "A Survey of Nonforest Products Industrial Wood Energy Users". Forest Products Journal 37(2): 57-61.

Zelenski, S.G., Pangaro, N. and Hall-Enos, J.M., 1980. "Inventory of Organic Emissions from Fossil Fuel Combustion for Power Generation". Prepared by GCA Corporation for Electric Power Research Institute. EPRI EA-1394, TPS 78-820.

Zierock, K., Rothe, G. and Steppat, R., 1983. "Polycyclic Aromatic Hydrocarbons in the Particulate Emissions of Three Diesel Engines". SAE Paper 830458. Society of Automotive Engineers, Warrendale, PA.